CHRONOLOGY OF RESEARCH AT NRRC ON ALCOHOL FUEL

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Alcohol

During the past fiscal year, the most important problem faced by the industrial and beverage alcohol industries involved the conversion of plant facilities and processes to the use of wheat as a raw material. Before the war, industrial alcohol was made from molasses as the principal raw material, while distilled liquors were produced principally from corn and rye grains. Conversion of the beverage alcohol plants to the use of wheat posed several serious problems, and the distilleries which used molasses faced the additional problems caused by lack of grain handling and grinding equipment.

Through cooperation with the industry, this Laboratory has played an important part in the solution of the various problems involved in conversion to the use of wheat. At the request of the War Production Board, two conferences have been held here (November 5, 1942 and February 25-26, 1943) for the purpose of solving these problems as quickly as possible. At the first of these conferences, which was attended by representatives from industrial, government, and university laboratories, the problems were discussed and an intensive short range research program was laid out with the assignment of certain phases of the work to each of the cooperating laboratories. All work was conducted on standard samples supplied by the Commodity Credit Corporation, and the results were reported to and coordinated by this Laboratory. At the second conference, discussion of the results revealed that most problems had been solved; recovery of by-product feeds and determination of their nutritive value remain as important unsolved problems on which work is being continued.

As its share of the cooperative research program, this Laboratory conducted a survey of its large collection of yeasts in order to select those best adapted to wheat fermentation. The three or four best organisms were selected and these are now available to industry. They do not require added nutrients and it has been demonstrated that with them, as good alcohol yields may be obtained from wheat as from corn on the basis of the starch contents of the grains. This is true of normal wheats as well as of rain damaged wheats from North Dakota and musty wheats from Illinois. The yield of alcohol may be raised significantly by the use of certain mold amylases.

Late in June, 1942, construction and erection of the 500 gallon-per-day alcohol pilot plant were completed. Several tests were conducted which showed the need for certain changes and improvements, which were completed with the final acceptance of the plant in November 1942.

Butylene glycol

Since the pilot plant was accepted it has been used to study the pilot scale conduct of butylene glycol fermentation. For this purpose further extensive changes in the equipment were necessary and therefore the studies on alcohol production have been temporarily suspended.

The fermentation of wheat mashes to 2,3-butylene glycol by Aerobacter Aerogenes and Bacillus polymyxa has been studied on laboratory and pilot plant scale. The results are substantially the same as those obtained from the fermentation of corn, except that the yield of products (butylene glycol plus acetylmethyl carbinol plus ethyl alcohol) is generally slightly lower from wheat than from corn.

The fermentation of acid-hydrolyzed wheat starch and acid-hydrolyzed granular wheat flour by Aerobacter Aerogenes has been studied intensively. A low efficiency of conversion of the starch content of such substrates to butylene glycol has been consistently observed, although good growth of the organism and an accelerated rate of glucose consumption are obtained. Increased production of ethyl alcohol is also associated with such anomalous fermentation. Investigation of the action of growth factors and trace elements in this process is underway, with the ultimate objective of devising means for obtaining high butylene glycol yields from starches and granular wheat flours.

A comprehensive statement on the results and significance of the work on butylene glycol is given in the project "Corn Utilization Investigations". The statement given there is also applicable to the project "Wheat Utilization Investigation".

Motor Fuels

For purposes of testing alcohol and alcohol blend motor fuels, the following installations were completed:

Two high speed Watkesha crankcases to be used with cylinder assemblies for -
ASTM D357-42T Test for knock characteristics of motor fuels
ASTM D614-41T Test for knock characteristics of aviation fuels
ASTM D613-41T Test for ignition quality of fiesel fuels
Army and Navy 3-C Supercharged aviation fuel test method (not all standard equipment)
Cylinder injection using Hesselman type
Supercharging with manifold injection

A 35 h.p., cradle type, D.C. dynamometer
A 15 k.w. motor generator set
An exhaust gas analyzer
Air and fuel intake, temperature and pressure measuring devices
Fuel dispensing rack, work benches, and miscellaneous equipment

Calculations have been made to determine the amount of alcohol necessary to prevent icing of aircraft carburetors under various weather conditions, and the conclusions are to be tested experimentally with apparatus now being assembled. When alcohol was used in a supercharged aviation fuel test procedure,

it was found necessary to add one percent of castor oil (perhaps less may serve) in order to provide lubrication of fuel injection pumps. A major difficulty in the rating of fuels in supercharged engines is the detection of knock. Neither the knockmeter, as used in the Motor Method, nor the thermal plug of the 1-C Aviation Method is satisfactory, and detection of knock by ear must be relied upon until other instrumental methods can be developed. Engine noise at high power output tends to obscure audible knock, and causes difficulty in distinguishing order of knock intensity. Using the oscillograph with high amplification of the output of a piezoelectric pressure pickup and a 60° angular sweep unit, it was found that audible knock registered as ripples near and at the pressure maximum. Adaptation of this observation to the determination of knock rating is under study.

Octane ratings of alcohol and alcohol-water solutions were determined and the correct ASTM value found to be 91, as compared to values of 90 and 99 O.N. reported in the literature. With a leaner mixture using the jet size for gasoline, a rating of 99 O.N. could be obtained. The addition of water to alcohol progressively raised the O.N. to a value of 99 O.N. at 15 percent water. Further increase in water content up to 25 percent did not affect the rating.

Investigations are in progress to determine the effect of certain additions to alcohol. These studies are designed to show the effects of impurities that might be expected according to the method of manufacture of the alcohol as well as the effects of materials deliberately added to the alcohol to modify some of its properties. Thus, an additive which would improve the knock rating of alcohol would be of value as tetraethyl lead does not affect alcohol rating. Ether in concentrations up to 15 percent by volume did not affect the alcohol rating as determined by available methods.

Motor method ratings are considered to be inadequate in the determination of fuel quality and must be supplemented by other laboratory and also road tests. Both benzene and alcohol are penalized in the 1-C Aviation Fuel Test as in the old Army Method. This test is only an intermediate between the Motor Method and the 3-C Supercharged testing procedure.

June 1, 1943, to May 31, 1944

Saccharification of Agricultural Residues

Studies on the kentics of hemicellulose hydrolysis from agricultural residues as the first step in a saccharification process were undertaken in 1940, but were temporarily discontinued because of the pressure of other work. They were reopened, however, in June 1943 because of the critical food situation and the need for nonfood raw materials for the production of ethyl alcohol.

Previous saccharification processes, chiefly dependent on wood as a raw material, have almost entirely neglected utilization of the hemicelluloses which are low in waste wood. Agricultural residues, on the other hand, contain considerable amounts of hemicellulose and are correspondingly lower than many wood species in cellulose. The manufacture of furfural or xylose sugar from hemicelluloses is known from previously developed processes. Development work on a process for the continuous short-cycle, low-temperature, concentrated-acid saccharification of agricultural residues was begun in June 1943; but this process consisted of the separation of the pentosan, cellulose, and lignin fractions so that monetary values might be realized from each. During the course of the investigation, more than 2,400 pounds of different agricultural residues were processed. Equipment capable of processing 80 pounds of residue per hour was used during the later large-scale laboratory development.

The last and semi-pilot plant work carried on to date on this process, together with the best preliminary cost estimates, indicates that, provided markets can be found for the furfural produced from the process at a price considerably below present price quotations, and provided a market can be found for lignin at 3/4 to 1-1/2 cents per pound, glucose can be made at a price to compare with black strap molasses. This, in turn, guarantees very low cost alcohol, butylene glycol, or other fermentation products, at low prices from a nonfood material source. Agricultural residues are particularly suited for the saccharification process because of the high yields of furfural or xylose which can be produced. This production can demand a price higher than glucose in present-day and in future markets.

Agricultural Motor Fuels

During the past year, many of the facilities of the alcohol pilot plant have been used for the pilot plant production of butylene glycol. This has prevented the utilization of this pilot plant for the production of alcohol.

During the year, however, a large number of alcohol blends have been tested using the A.S.T.M. Motor Method and the Research Method. Neither method gives satisfactory agreement with road tests, though the latter procedure is more amenable to the so-called sensitive fuels such as aromatics and alcohol. In spite of this lack of agreement, these methods give considerable information on a comparative basis. Since alcohol has a negative lead susceptibility, it was of importance to find out the action of lead in blends as well as to attempt to find a compound which will have an effect in alcohol fuels similar to that which tetraethyl lead has in gasoline.

Extensive use has been made of the supercharged aviation test procedure (F-4) for testing agricultural motor fuels. Information concerning this method is at present restricted and any results or discussion given are therefore confidential. So far, it has not been possible to apply this method strictly to agricultural motor fuels, since "engine roughness" rather than "light knock" is being used as the test criterion.

A very complete calculation has been made to compare the thermodynamic properties of producer gas obtainable from agricultural materials with those of alcohol and gasoline when used in internal combustion engines. It was found that supercharge rather than increase in compression ratio is a more suitable method to obtain power equivalent to that obtainable from either alcohol or gasoline.

One criticism of alcohol fuels is their supposedly corrosive nature. Extensive laboratory tests preparatory to engine tests have therefore been made and are being continued to investigate the corrosion resistance of copper, brass, aluminum, cast iron, galvanized iron, and steel to various agricultural motor fuels. The experiments are designed to imitate conditions existing in the fuel system, including tank, lines, pump, carburetor intake manifold, as well as in the cold engine cylinder after combustion.

Wheat Alcohol

During the previous year, the Northern Regional Research Laboratory was requested to coordinate all research on the production of ethyl alcohol from whole wheat and wheat flour. During that year, two conferences were held on this subject and a third was called for September 27, 1943. At this conference it was concluded that the objectives of the coordinated research had been accomplished and that the outstanding problems in the use of wheat for the production of ethyl alcohol had been worked out. The Laboratory was selected to coordinate and summarize the reports which were submitted by all the participating agencies. In closing this project, a 30-page summary report of the entire research was prepared and sent to the War Production Board for distribution. This report included abstracts of all reports submitted by the various cooperating agencies.

April 1, 1944 to March 31, 1945

Saccharification of Agricultural Residues

The joint report by the Agricultural Residues Division and the Engineering and Development Division of this Laboratory recommending the operation of a continuous process for the saccharification of agricultural residues on a pilot-plant scale was reviewed by the Forest Products Laboratory at the request of the Chief of this Bureau. Based on the recommendations of the Chief of the Bureau, the Secretary of Agriculture requested from the Secretary of the Interior an appropriation of $410,000 for building a semi-works plant and for undertaking a complete study of the process on a semi-works scale as a part of the program for the development of synthetic liquid fuels from non-petroleum sources authorized by the 78th Congress under Public Law 290, April 5, 1944. This sum was authorized to be transferred to the Secretary of Agriculture early in the summer and on November 1, 1944, a separate project, known as Synthetic Liquid Fuels Investigations, was set up, reporting directly to the Chief of the Bureau. Dr. E. C. Lathrop of this Laboratory was appointed consultant on this project. The work by the Laboratory prior to November 1 on the saccharification process was chiefly concerned in the design of the equipment required in a semi-works operation capable of producing 2,000 pounds of glucose in 10-percent solution, 1,600 pounds of xylose in 15-percent solution, 200 pounds of furfural, and 1,000 pounds of lignin residue from 3.3 tons of agricultural residues, such as corncobs, in an 8-hour day. A paper discussing the process was presented as a part of the "Wood Sugar Symposium" at the meeting of the American Chemical Society in New York, September 1944.

Agricultural Motor Fuels

Due to the fact that during the past year many of the facilities of the alcohol pilot plant have been used for the pilot plant production of butylene glycol, it has been necessary to return the plant to its original condition, which has taken both time and energy. In the meantime, work has continued in the study of various methods of saccharification, on the production of vitamin products, and on the testing of motor fuels.

Saccharification.- In the experimental program on the replacement of malt for saccharification, fermentations were carried out with (a) malt under various conditions of cooking, (b) additives to improve the efficiency of malt, (c) fungal amylases, and (d) acid as the saccharifying agent.

(a) Influence of Cooking Upon Malt Saccharification.- It was found that by the application of a double cooking procedure great improvement could be obtained in saccharification. According to this procedure, an extract of the malt was withdrawn and reserved for the saccharification step. The cooking of the grain to be fermented was then done in two steps, using one-half the malt grains as premalt preceding each cooking period. It was found that when this was done and the malt extract added to the cooked and cooled mash, saccharification proceeded very rapidly, usually being complete within one hour. Mashes so prepared fermented to completion in approximately 40 hours and gave slightly higher yields of alcohol than mashes prepared by the conventional malting practice.

(b) Malt Adjuncts.- Marked acceleration of fermentation can be effected by adding the proteolytic enzyme, papain, to the cooked grain mash during the malting period. Papain appears to stimulate alcoholic fermentation by degrading grain protein to more assimilable forms of nitrogen. Preliminary work has indicated that proteolytic enzymes produced by Bacillus scaber cultured in thin stillage are capable of replacing papain.

(c) Fungal Amylases.- In an attempt to find sources of amylolytic enzymes which can completely replace malt, a survey has been made of the amylases produced by approximately 150 fungi cultured in thin stillage. Several strains have been found which form significant quantities and these enzymes are being employed in fermentation studies.

(d) Alcohol From Acid-Saccharified Grains.- The fermentation of acid-saccharified grains to alcohol has been investigated in both semi-pilot plant and pilot plant equipment. The conditions previously established for the saccharification of grains in the production of butylene glycol have been found to be satisfactory for alcohol fermentation. Yields of alcohol from corn have varied from 4.9 to 5.3 proof gallons per bushel. Wheat and rye have also been fermented satisfactorily after acid hydrolysis.

Motor Fuel Testing Investigations.- Investigations under this head have included a study of vapor lock in alcohol blends, the solubility of water in hydrocarbon alcohol blends, the use of iron pentacarbonyl with alcohol motor fuels, and the testing of several possible motor fuels prepared from furfural.

Investigations on the solubility of oxygen and nitrogen in motor fuels have shown that these gases are less soluble in the agricultural motor fuels than in the petroleum-base motor fuels. Therefore, vapor lock due to air dissolved in the fuel would be less likely to occur with agricultural motor fuels than with gasoline. It has also been found that the solubility of water in hydrocarbon-alcohol blends is such that in the case of gasoline blends containing 10 per cent of alcohol the addition of a stabilizer is not necessary. Through normal exposure in handling and distribution, the blend would not take up enough water to cause separation.

It has been found that iron pentacarbonyl will improve the octane rating of alcohol as tetraethyl lead improves gasoline. This compound substantially improves the octane rating of alcohol, but a way to overcome its tendency to cause deposits in the engine must be found before it can be recommended for use.

The Laboratory joined the Chicago Area Aviation fuel exchange group which was one of the regional groups formed at the urgent request of the Petroleum Administration for War. Samples are being exchanged, and meetings, the most recent of which was held at the Northern Regional Research Laboratory, are scheduled for each month at one of the cooperating laboratories.

April 1, 1945 to March 31, 1946

Fermentation Studies on Xylose

Fermentation studies were conducted on the xylose obtained from the hydrolysis of corncobs. It has been shown that xylose in 1 and 2 percent concentrations fermented rapidly and completely to acetone butanol, and ethanol. With xylose concentrations between 3 and 5 percent, however, fermentation was slow and incomplete, e.g., 60 to 70 percent being fermented within 5 days. To study this fermentation more thoroughly, xylose varying in purity from that present in crude hydrolyzates to that which had been recrystallized was fermented in concentrations from 1 to 5 percent. It was found that more than 90 percent of the xylose in all concentrations was fermented when the crude hydrolyzate was treated with activated carbon. Crystalline xylose and the untreated crude liquors fermented poorly. This and subsequent experiments indicated that activated carbon removes an inhibitory principle but apparently leaves some essential substance in the treated liquor which improves fermentation. Further studies are being carried out along these lines. It is now possible to ferment xylose satisfactorily to acetone, butanol, and ethanol when it is the only sugar present and levels up to and including 5 percent are employed.

ALCOHOL AND OTHER LIQUID FUELS

Saccharification

In the experimental program on the reduction of saccharification costs, fermentations were carried out with (a) additives to improve the efficiency of malt, and (b) fungal amylases.

(a) Malt adjuncts: Papain and other proteolytic enzymes have been shown to stimulate alcoholic fermentation.

In a study made of the effects of adding individual as well as complete mixtures of amino acids to alcoholic fermentations, it was found that no single amino acid gave more stimulation than might be expected from the added amino nitrogen. Mixtures of amino acids such as those contained in casein hydrolysates, however, gave excellent stimulation comparable to that imparted by papain.

(b) Fungal amylases: In an attempt to find sources of amylolytic enzymes which can completely replace malt, a survey has been made of

amylases produced by 250 fungi cultured in thin stillage. Several strains have been found which form significant quantities and these enzymes are being employed in fermentation studies. One culture especially elaborates unusual quantities of amylase. Culture filtrates from this organism can totally replace malt in the alcohol fermentation of corn when used in a method developed at this Laboratory.

Studies on the production, utilization, and evaluation of a fungal amylolytic material for the conversion of starch to fermentable sugars were continued on a pilot-plant scale. During this period many experiments were conducted in which the mold was grown by submerged fermentation on thin slop fortified with corn and calcium carbonate. The enzymatic liquor was prepared in 400-gallon batches, portions of which were used to saccharify 800-gallon batches of grain mashes, and the converted mashes were then fermented with yeast in the usual way. The yields of alcohol were compared with the yield obtained from a fermented mash that had been saccharified with barley malt.

The adjunct requirements of thin slop for optimum production of amylolytic activity were investigated. It was found that a very satisfactory medium could be prepared by the addition of as little as 1 percent ground corn and 0.5 percent calcium carbonate to thin slop. When the mold is grown on this medium the enzyme activity of the liquor reaches a high level in 3 days.

Laboratory data indicated that a concentration of amylolytic liquor amounting to 20 percent was required for the conversion of grain mashes, i.e., 20 gallons of liquor to produce 100 gallons of converted mash. The recommended conversion temperature was 130° F. Many mashes were converted and subsequently fermented to alcohol with the yield averaging 5.25 proof gallons per bushel of corn containing 12 percent moisture. The highest yield was 5.40 proof gallons. The proportion of liquor used for conversion was reduced first to 15 percent, then to 10 percent, and recently to 7 percent, with satisfactory results. Fermentations are complete, usually in 48-60 hours. Because of contaminants in the mold preparation, the temperature of conversion was raised to 140° F. in order to prevent the pH from becoming too low during the fermentation. There appears to be no loss of amylolytic activity, and with this procedure the pH at the end of the fermentation is usually above 4.0.

It has been determined that the yields of alcohol from the fermentation of mashes converted with 10 percent malt or with a liquor containing mold amylase are comparable. There are indications that fermentations in which mold enzymes have been the saccharifying agent give slightly higher yields of alcohol; perhaps 0.1 proof gallon per bushel.

Physical Studies

Studies of the stability of alcohol-gasoline blends for various hydrocarbon-water mixtures have shown that, providing precautions are taken, blends containing 10 percent, or more, of ethanol are stable.

The solubility of oxygen and nitrogen in ethanol and other possible fuels has been determined, prompted by the fact that dissolved gases may be the cause of vapor-lock in aviation fuel systems, and this probably in systems used on the ground.

Vapor pressures and densities of ethanol-isooctane mixtures have been measured as a necessary step in the Laboratory's comprehensive determination of liquid-vapor relationships of ethanol-hydrocarbon systems.

Alcohol-Water Injection

Investigation of injection of alcohol and alcohol-water mixtures into the intake manifold of automobile engines has not been completed, but studies show engine performance can be improved by this method. A relatively high compression ratio, lean carburetor adjustment, and a fuel of lower octane rating than could ordinarily be used successfully under these conditions seem to give best results. Road tests and further laboratory work will be necessary to draw up recommendations.

Corrosion

It has been shown that a large number of metals and alloys, such as might come in contact with motor fuels, when exposed to a 10 percent ethyl alcohol-commercial gasoline blend, do not corrode to any serious extent, nor to an extent greater than when exposed under similar conditions to commercial gasoline.

April 1, 1946 to March 31, 1947

ALCOHOL AND OTHER LIQUID FUELS

Synthetic Liquid Fuels Investigations

The research work under the Synthetic Liquid Fuels Project is closely coordinated with that of the Northern Laboratory, which, since its founding, has been engaged on various phases of the problem of fuels from agricultural products.

The purpose of the Synthetic Liquid Fuels Project is to determine the manufacturing steps and costs on a semi-works scale of a process for the hydrolysis of agricultural residues to sugars, in solution of high concentration, and to lignin. The motor fuels testing laboratory is investigating the value of fuels produced from the sugars, from furfural, or from lignin. Investigations on crystallizing xylose or glucose from the sugars, the development of chemical derivatives from the sugars or from furfural, as well as uses for lignin, other than for fuel, are being undertaken by this Laboratory. Progress to date has been quite satisfactory.

Butyl Alcohol Fermentation of Xylose Liquors

It has been found possible to ferment xylose saccharification liquors obtained through the hydrolysis of corncobs to butyl alcohol, acetone, and ethyl alcohol. Of a variety of treatments studied it was found that charcoal treatment materially improved the saccharification liquors for fermentation. If, in addition, reduced iron was added in small amount, good fermentation of the liquors was guaranteed. Reduced iron serves both to reduce the oxygen tension of the medium and also to remove excess copper which is introduced through corrosion of the bronze equipment used in making the hydrolyzates.

Fermentation of the hydrolyzates could be obtained in many cases without pretreatment with carbon, provided reduced iron was used. Some other commercial preparations of finely divided iron have also been found effective in making the liquors fermentable. Work on this fermentation has now started in the alcohol pilot plant.

Satisfactory operating conditions have been determined for the sterilization of xylose liquor in the pilot plant. Preliminary large-scale fermentation experiments have been only moderately successful, but the results indicate that a satisfactory process can be developed.

Motor Testing of Synthetic Liquid Fuels

Since from the standpoint of motor testing, the liquid fuels derived from agricultural residues usually are the same as those derived by fermentation of cereal crops comprising such substances as alcohol, furfural, butyl alcohol and acetone, all studies on this subject will be given under the report on "Corn, Wheat, and Other Cereal Crops Utilization Investigations" with the same title of "Alcohol and Other Liquid Fuels."

Publication of a bibliography on "Construction, Design, Economics, Performance, and Theory of Portable and Small Stationary Gas Producers" has aroused unusual interest. The Wellman Engineering Company, Cleveland, Ohio, has built a large gas generator for internal combustion engines, designed for use of agricultural residues as fuel. It is understood that although this unit is to be sold to South American interests, the company is looking for a market also in this country.

Kinetics of Combustion

In continuation of previous studies of ethanol-hydrocarbon systems, the density of ethanol and the thermal expansion and vapor pressure of the ethanol-isooctane system have been measured with great precision. Preliminary studies on the kinetics of combustion have been made and analytical methods surveyed for use on this problem. A very extensive summary of published work on alcohol as a motor fuel has been completed and arrangements are being made for its publication.

ALCOHOL AND OTHER LIQUID FUELS

Motor Tests

To evaluate new motor fuels properly, studies must be made on many physical properties such as density and vapor pressure, not only for the mixed fuel but also for the pure components. Other factors such as gum stability and corrosiveness must be measured. After a full program of such laboratory studies, the final test of motor fuels is given by road tests. Many blends of alcohol with gasoline have been studied by use of the single-cylinder test engine, and, for a full-scale dynamometer test, by use of a 1941 Plymouth engine. Fuels studied included two standard gasolines with amounts of alcohol from 10 to 50 percent pure alcohol, and blends containing benzene. Many factors such as specific fuel consumption, efficiency, brake horsepower, etc., were evaluated for all of these fuels.

As a brief and incomplete summary of this work it may be stated that best performance for high-alcohol blends requires higher compression ratios than 7.3; with standard carburetor jets, 25-percent alcohol gives highest efficiency, but pure alcohol the most power; engine roughness occurs only for blends containing more than 50-percent alcohol and may be reduced by manifold heating (with some power loss); for pure alcohol, fuel injection seems preferable.

Fungal Enzymes

It has been demonstrated that a number of species of *Aspergillus* are capable of producing high levels of α-amylase when they are cultured by deep vat procedures. The filtrates may be used to saccharify grain mashes with the subsequent production of high alcohol yields. It was noted that good alcohol yields did not depend only upon α-amylase production, but also upon the maltase activity of the filtrates.

Species of *Aspergillus* (for example, *Aspergillus niger* NRRL 679) which produced high levels of maltase activity, as well as α-amylase activity, resulted in more rapid alcoholic fermentations when filtrates of their cultures were used as saccharifying agents. Fungal amylase systems containing good maltase activity rapidly converted starch, dextrins, and maltose to glucose, whereas malt degraded starch to dextrins and maltose and then only slowly to glucose. Crude filtrates of a number of mold cultures have been investigated for ability to hydrolyze various polysaccharides. In general it was found that all mold filtrates studied were capable of hydrolyzing maltose, inulin, sucrose, and the α-limit dextrin obtained from potato amylopectin. None of the mold filtrates studied were capable of hydrolyzing lactose, α-methyl-d-glucoside, levoglucosan, calcium lactobionate, and calcium maltobionate. A filtrate from one culture was slightly active on trehalose, and that from another was capable of hydrolyzing cellobiose.

The use of fungal amylase as a replacement for malt in alcoholic fermentations has been carried out successfully on a pilot-plant scale.

Five of the most promising strains of *Aspergillus niger* studied in the laboratory have been tested in the pilot plant for use in the production of alcohol. Experiments have been conducted in which the fungi were grown by submerged fermentation on thin slop fortified with 1 percent ground corn and 0.5 percent calcium carbonate. The enzymatic liquor produced was used to saccharify 1,200-gallon batches of grain mashes and the converted mashes were fermented with yeast in the usual way. The amount of liquor used was such that it constituted 10 percent of the mash that was fermented.

Two strains, namely, *Aspergillus niger* NRRL 330 and NRRL 337 were used in series of experiments in which each fungus was grown in thin stillage obtained from the fermentations where it had been used as the saccharifying agent. These particular fungi have been utilized through five cycles with no diminution in the yields of alcohol. On the average, the yields of alcohol amounted to 5.1 proof gallons per bushel of grain fermented.

This process has been adapted to a semi-commercial scale by two companies in the alcohol industry and to a pilot-plant scale by a company interested in producing fungal amylase for use in the manufacture of sweetening agents.

April 1, 1947 to March 31, 1948

Fungal Amylase by Submerged Culture

The yield of alcohol from the fermentation of corn mashes saccharified with mold culture filtrates appears to correlate more closely with the maltase than with the α-amylase activities of fungal enzyme preparations. By slightly modifying the media formerly used, the maltase activities were increased. The use of such high potency fungal enzyme preparations permitted a substantial reduction in the amount required to saccharify the corn mash and still give the same yield of alcohol on subsequent fermentation with yeast. When equal quantities of enzyme preparations were used, higher yields of alcohol resulted from the use of the preparation higher in maltase.

Several distilleries are now investigating the use of submerged fungal enzymes as saccharifying agents. A report from one of them on the use of Aspergillus niger NRRL-337 appeared in Ind. Eng. Chem. 39 1615 (1947). Increased yields of alcohol from the fermentation of corn mashes saccharified with fungal enzymes over malt controls were consistently obtained, thus confirming our laboratory and pilot-plant findings.

The removal of undesirable protein cleavage products and ash from fungal enzyme preparations is generally necessary prior to their use in sirup or similar food manufacture. To obviate this necessity an economical protein-free synthetic medium for submerged production of potent fungal enzyme preparations is being developed. The resultant culture filtrates so far obtained have been odorless and tasteless and have had a light straw color. Fungal enzymes thus prepared may possibly be used directly in the food processing industry.

Sulfur in Motor Fuel in Relation to Alcohol Blends. Single Cylinder Tests

Sulfur in gasoline is especially undesirable because it adversely affects added lead tetraethyl. Preliminary studies on the effects of various sulfur compounds in blends, with and without added lead have been made with the single-cylinder CFR engine. These tests have shown an apparent reduction in the adverse effect of sulfur when ethanol was blended with the standard reference fuel used. An extensive evaluation of this effect has been started in which the effects of four types of sulfur compounds in a reference fuel of gasoline and five blends (including ethanol and butanol) will be studied.

Synthetic Liquid Fuels Investigations

The research work under the Bureau's Synthetic Liquid Fuels Project is closely coordinated with that of the Northern Laboratory. The process for hydrolyzing agricultural residues to sugars for conversion into liquid fuels basically consists of converting one of the fractions of agricultural residues, pentosans, to pentose sugars and, subsequently, converting the cellulose fraction to dextrose. The pentose sugars may be fermented to the liquid fuels, butanol, acetone, isopropanol, and ethanol, or they may be converted to furfural. The dextrose, of course, may be fermented to the liquid fuel, ethanol.

A semi-works plant for studying this process has been in operation for about one year. Approximately 400,000 pounds of cobs have been processed. One hundred runs of 4,000 pounds of cobs each have indicated that pentosans in corncobs may be hydrolyzed in 93-percent yields to conversion products, 87 percent of the pentosans being converted to pentose sugars and 6 percent to furfural. Since cobs contain about 32 percent pentosans, a little more than 600 pounds of pentose sugars may be produced from one ton of dry cobs. These methods of producing pentose sugars are presently being used by two industrial concerns. One concern is producing crystalline pentose sugars on a small scale, and the other is investigating the production of both pentose sugars and dextrose from corncobs. The second step in the semi-works plant for converting cellulose to dextrose is now under study.

The Butanol Fermentation of Pentosan Hydrolyzates

Accumulated data on certain factors characterizing the fermentation of pentosan hydrolysis liquors to butanol, acetone, and ethanol have permitted considerable simplification of the fermentation mash and procedure. Control of the initial oxidation-reduction potential of the medium to insure anaerobic conditions has proved necessary for satisfactory fermentations. Once the bacteria start to proliferate, their metabolic activities maintain the necessary reducing conditions. Copper, resulting from mild corrosion of the hydrolysis equipment, and at least one other unidentified toxic factor, are present in the pentosan hydrolyzates and deleteriously affect the multiplication of organisms. On the other hand, substances beneficial and essential to the fermentation are also present. Removal of the toxic principles alone from the liquors prior to fermentation has been found possible. This could be accomplished successfully in small flasks by direct addition of iron powder to the fermentation medium, but this procedure met with serious mechanical difficulties in the pilot plant. It was found that if the iron were used in an adequate pretreatment of the hydrolyzate liquors, then the iron could be omitted from the fermentation medium. It was further found that some of the other chemicals

previously used were also unnecessary. The cost of chemicals required to supplement the pentosan hydrolyzate liquors has thus been reduced from 2.43 cents to 0.35 cents per pound of mixed solvents produced. The chemicals now used are only to furnish assimilable nitrogen and phosphate for the bacteria. An economical and practical procedure to remove only the deleterious substances is now being developed and will be installed as a pretreatment step preceeding fermentation in pilot-plant operations.

An industrial butanol fermentation concern has evidenced considerable interest in the process and will shortly test it in their plant.

Motor Testing of Synthetic Liquid Fuels

An extensive series of tests on a 1942 (Chevrolet) engine were completed. Blends containing from 5 to 15 percent alcohol were tested under motor loads corresponding to actual driving conditions. It was found that use of these blends may require only use of a "rich jet" in the carburetor for the higher blend to produce satisfactory and efficient performance. Similar tests were also made on a high-speed 1947 engine (Crosley) at normal and 9:1 compression ratio. Regular gasoline with 20 percent alcohol and premium gasoline with 10 percent alcohol were sufficiently improved to equal the performance of 90 octane (Motor and Research Method) gasoline required at the high compression. Use of alcohol water injection was given preliminary tests and evaluation with such promising results that an expanded project under Research and Marketing funds was established.

April 1, 1948 to March 31, 1949

The Fermentation of Pentosan Hydrolyzates to Solvents

Various methods of fermenting pentosan hydrolyzates to butanol and its associated products in media not containing iron powder have been investigated. The use of a tower packed with iron powder to remove inhibitory materials from neutral hydrolyzates presented serious mechanical difficulties on pilot-plant scale. The necessity of having iron present in the fermentation medium can also be obviated by incorporation of corn, corn steep liquor or grain alcohol stillage. Laboratory studies have demonstrated that supplementation of pentosan hydrolyzates with corn so that the latter supplies 25 percent of the total sugar in the medium permits satisfactory fermentations. Alternative methods of supplementing pentosan hydrolyzates include the use of corn steep liquor at 2 percent (dry basis) concentration in the fermentation medium or the use of distillers' thin stillage as the diluent to reduce the sugar content of pentosan hydrolyzate sirups to fermentation levels. If the corn required to supplement pentosan hydrolyzate can be held to 25 percent, or less, of the total sugar in the medium, the process appears to be economically feasible. Fermentations of mixtures of corn and pentosan hydrolyzate are currently being carried out in 3,000-gallon quantities in the pilot plant to check laboratory findings.

Full-scale Engine Studies--Alcohol Blends

The automatic setup for wear measurements is in operation. Thirty-five-hour runs are being made using a 15-minute cycle divided into 3-minute idling period, a 7-minute, 40 m.p.h. (2,100 r.p.m.) road load period and a 5-minute cooling period during which the jacket temperature changes from 140° F. to 46° F. Wear measurements will be referred to gasoline.

Physical Chemical Studies

Results on the vapor in liquid equilibrium of ethanol-toluene mixtures will appear in the April issue of the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, and similar data for ethanol methylcyclohexane solutions are in the hands of the editor.

The corrosion of metals, as well as the prevention of corrosion by means of inhibitors in the presence of alcohols, alcohol-water mixtures, and denaturants is being studied extensively. Metals included in the study are aluminum, brass, copper, iron, lead, magnesium, nickel, solder, tin, and zinc, as well as their combinations.

Production and Utilization of Fungal Amylase

It has been found that the alpha-amylase and maltase yields from submerged cultures of Aspergillus niger NRRL 337 may be controlled by varying the quantities of stillage solids (from the ethyl alcohol fermentation) and of corn used in the mold propagation medium. Increasing the stillage solids concentration raises the yield of alpha-amylase; increasing the corn concentration raises the yield of maltase. The higher yields of enzymes now obtainable permit the use of proportionately lower amounts of the fungal amylase preparation for conversion of grain mashes. Although 3.6 gallons of fungal amylase were recommended previously for the conversion of a bushel of grain in the alcohol fermentation, 2.9 gallons and even less of the improved mold enzyme preparations have been used successfully.

The optimum temperature for the conversion of grain, as assayed by alcohol yields from fungal amylase-saccharified mashes, ranges from 55° to 65° C. The higher the temperature, the shorter should be the conversion time. "Malting" with fungal amylase at the higher temperatures and shorter times does not increase the alcohol yields over those secured at the lower temperature, but it does improve the liquefaction of mash. In plant operation where the viscosity of mash is an important factor affecting pumping costs, conversion at the higher temperatures would appear advantageous.

Single Cylinder Octane Rating Tests

The Motor (M.M.) and Research (R.M.) octane numbers of four representative gasolines straight and with 0.5, 1.0, 1.5, and 2.0 ml. tetraethyl lead per gallon were measured plain and blended with 10, 25, and 35 percent of ethanol, 10, 25, and 35 percent ethanol-methanol (50:50 mixture) and with similar combinations in presence of water. The M.M. and R.M. octane numbers for one selected gasoline plain and blended with 10, 25, and 35 percent ethanol are 74.0, 84.3; 79.5, 90.1; 84.6, 97.5; 88.5, 100 (isooctane) + .11 ml. tetraethyl lead, respectively. The same values with addition of 0.5 ml. T.E.L./gal. are 79.7, 89.0; 83.7, 95.2; 85.7, 100 (isooctane) + 1.2 ml. tetraethyl lead; 88.2, 100 (isooctane) + .37 ml. tetraethyl lead, respectively. At least two conclusions may be drawn from these results: (1) With small amounts of lead (0.5 - 2.0 ml.) the increase in Research Octane number is large enough even in blends up to 35 percent alcohol to warrant its inclusion for the highest octane gains; (2) both alcohol and lead in combination or alone effect the Research Octane number to a much greater extent than the M.M. octane number; (3) relatively small gains in the high octane range are still significant and lead may give the extra boost in the extreme range; (4) at the higher compression ratios the R.M. octane number appears to have the greater significance; however, the present confusion resulting from the varied composition in gasoline make it difficult to predict the behavior of motor fuels unblended or blended. Gasoline manufacture is in a status of flux and running tests must be made to keep up with the ever-changing picture.

A total of 15 sulfur compounds including various mercaptans, sulfides, disulfides, and paraffins were studied in a number of alcohol blends. Results indicate that the presence of alcohol has a slightly inhibiting effect on the lowering of the octane number of leaded hydrocarbons by sulfur compounds. Unleaded alcohol hydrocarbon blends containing sulfur are effected to a slightly greater extent than a similar unleaded hydrocarbon.

April 1, 1949 to March 31, 1950

Fermentation of Pentosan Hydrolyzate Liquors:

(RRL-5-(3)-E-3-1 and F-5-1) Work is continuing on the fermentation of pentosan hydrolyzates derived from acid hydrolysis of corncobs.

Pilot-plant scale investigations indicate that satisfactory yields of butanol, acetone, and ethanol can be obtained when the butanol fermentation is conducted on 75:25 percent mixtures of pentosan hydrolyzate and corn. Yields of 0.25 pound of mixed solvents per pound of sugar (in the form of pentosan hydrolyzate and/or corn) charged to the fermentor have been obtained consistently, but five or more days are required for the fermentation to go to completion. In an effort to reduce the time of fermentation by acclimating the fermenting organism to the medium, fermentation has been initiated on corn alone, after which the hydrolyzate is added slowly to the fermenting corn mash. No reduction in time has been accomplished to date by this procedure, but additional modifications of the fermentation method are now being studied to achieve this result.

(RRL-5-(3)-F-5-1) A limited number of samples of pressure-cooked pentosan hydrolyzates prepared in bronze cookers on a laboratory scale have been tested for fermentability. Results of fermentation trials in various media indicate that the fermentation characteristic of pressure-cooked hydrolyzates is substantially different from that of atmospheric pressure-cooked pentosan hydrolyzates. The former thus far have been more difficult to ferment than the latter.

Publication: Fermentation Process. By H. M. Tsuchiya, A. F. Langlykke, and J. M. Van Lanen. U. S. Patent No. 2,481,263. Sept. 6, 1949.

Spectrophotometric Method for Determination of Furfural: (RRL-5-(3,7,8)-A-2-1)

A spectrophotometric method for the determination of furfural has been developed which is both rapid and specific. The saving in time resulting from this method extends to all investigations which require the determination of furfural. For example, analytical procedures for the determination of pentoses or pentosans in plant materials involve the conversion of pentose to furfural and measurement of the furfural produced. The method is especially valuable to our research on the fermentation of pentosan hydrolyzates, where, because of the toxicity of furfural to fermenting microorganisms, routine measurement of the furfural content of the pentosan hydrolyzates must be made.

Single Cylinder Engine Tests: (RRL-5-(3,7,8)-MFE-1-1)

Preliminary work indicated the possibility of using a single cylinder, stationary engine in tests to approximate road behavior of fuels, and thus assist in screening fuels for actual road tests. The method is now being studied cooperatively under the auspices of the Coordinating Research Council.

To compare relative engine wear and engine deposits using gasoline, gasoline-alcohol blends, and two different gasoline-denatured alcohol blends, 100-hour runs were made with the single cylinder Lauson engine. No detrimental effects in terms of engine wear or deposits were noted for the alcohol denaturants tested.

Octane numbers were run, using both the "Research" and "Motor" methods, on regular and premium gasolines of the more common brands, blended with alcohol. Satisfactory responses to blending were obtained.

Full-Scale Engine Studies: (RRL-5-(3,7,8)-MFE-1-2)

Following preliminary trials, four 200-hour tests on engine wear were run in full-scale stationary engines using gasoline and a 25 percent denatured alcohol blend with gasoline. Average wear data, obtained from a total of 64 indentations in the cylinder walls made at four levels of piston travel gave .0003 inch of wear for the 25 percent blend and .0005 inch for the gasoline, indicating that the alcohol blend produced less wear, and that the denaturant used, ST-115, was not harmful under test conditions. Results were very consistent in each of the two sets of test runs.

Three 10,000-mile runs with a 25 percent denatured alcohol blend with gasoline showed a fluffy carbon deposit in the combustion chamber in contrast with a harder carbon deposit formed with gasoline alone.

Physical Chemical Studies: (RRL-5-(3,7,8)-MFE-1-3)

An apparatus has been set up for the accurate determination of solubility of ethane, propane, n-butane, isobutane, and n-hexane in the lower alcohols. Such mixtures show exceptionally good water stability.

Tests are being carried out to determine accurately the corrosion resistance of certain metals toward ethanol and methanol in the presence of water, acetic acid, acetaldehyde, ethyl acetate, and various hydrocarbons. Copper, aluminum, iron, tin, and zinc are the metals being tested, with other metals to be added to the test later. A preliminary summary of results is being prepared. The best corrosion inhibitor found for ethanol-water mixture appears to be morpholine (diethylene-imide-oxide), a compound readily available at a reasonable price.

Suitability of several alcohol denaturants for injection mixtures and alcohol-gasoline blends are being tested.

Publications: U. S. Department of Agriculture Bibliographical Bulletin No. 10, The Technical Literature of Agricultural Motor Fuels. By Richard Wiebe and Janina Nowakowska. 289 pp. February 1949.

Liquid-Vapor Equilibrium of Ethanol-Toluene Solutions. By Carl B. Kretschmer and Richard Wiebe. Jour. Amer. Chem. Soc. 71: 1793-97. 1949.

Liquid-Vapor Equilibrium of Ethanol-Methylcyclohexane Solutions. By Carl B. Kretschmer and Richard Wiebe. Jour. Amer. Chem. Soc. 71:3176. 1949.

Alcohol from Agricultural Sources as a Potential Motor Fuel. By G. E. Hilbert. AIC-233. 7 pp. (Processed.) May 1949.

Production and Utilization of Fungal Amylase

(RRL-5-(7)-F-4-7):
A synthetic medium for the production of fungal maltase in submerged, aerated cultures of Aspergillus niger NRRL 330 has been developed in the laboratory. Yields of the order of 20 maltase units per ml. of culture, which compares favorably with the production of maltase in corn and grain alcohol stillage medium, have been obtained.

The filtrate of the culture from the synthetic medium used for the production of maltase was vacuum concentrated at 38° C. to about one-tenth the original volume without loss of enzymatic potency. Treatment of the sirup with calcium chloride effectively removed oxalic acid occurring in large amounts in the culture. Further purification was attempted by dialysis and electrodialysis. However, the occurrence of a potent cellulase interfered with such procedures. The Webb cell dialyzer proved absolutely useless because of the deterioration of the cellophane membrane. Greater success was met with a modified Brintzinger electrodialyzer, but even with this apparatus, samples were often lost. Nevertheless, dry preparations approximately 100,000 maltase units per gram have been obtained through electrodialysis and ethanol precipitation procedures.

Investigations on the ammonium sulfate precipitation of maltase are currently under way. Dry preparations approximately 65,000 maltase units per gram have been obtained.

The culture filtrate was capable of hydrolyzing isomaltose. This is of considerable interest since the linkage between the two glucose residues is of the α-1,6 type. This type of linkage occurs at the points of ramification of the amylopectin molecule and is resistant to the action of the common amylolytic enzymes.

Publication: Hydrolysis of the α-1,6 Glucosidic Linkage in Isomaltose by Culture Filtrate of Aspergillus Niger NRRL 330. By H. M. Tsuchiya, E. M. Montgomery, and J. Corman. Jour. Amer. Chem. Soc. 71 (9):3265. 1949.

(RRL-5-(3,7)-E-3-2): Experiments have been conducted in the pilot plant to determine the suitability of various grains for use in the production of ethyl alcohol with fungal amylase as the converting agent.

Moldy corn, hard and soft wheat, and sound grain sorghum have been utilized in these studies. The enzymatic liquor in all of the experiments was produced from thin stillage with a solids content of 4 percent to which had been added 5 percent of corn, wheat, or sorghum meal. In the studies using moldy corn, satisfactory fungal amylase liquors were produced when the medium was aerated at a rate of 1/4 volume of air per minute per volume of liquor. For the other grains, it was necessary to increase the rate of aeration to 1/2 volume of air per minute per volume of medium.

For all of the grains that have been tested thus far, yields of alcohol obtained with fungal amylase as the converting agent were at least equal to those obtained by the use of malt. No operating difficulties were encountered in any of the tests.

April 1, 1950 to March 31, 1951

Fermentation of Pentosan Hydrolyzate Liquors: (F-5-1 and E-3-1)
(Work on F-5-1 was discontinued July 1, 1950)

Satisfactory yields of butanol, acetone, and ethanol were obtained by the fermentation of mixtures of pentosan hydrolyzate and corn where the former supplied 75 percent and the latter 25 percent of the sugar. These fermentations, however, required 120 hours for completion. Such a fermentation time is generally considered too long to make the process practical.

Laboratory and pilot-plant investigations were conducted in an effort to reduce this time to 72 hours. It was thought that this might be accomplished by better acclimating the organism to the final medium to be fermented. Previously, the inoculum was prepared from a mash containing only corn and the necessary nutrients. Two other types of inocula were then tested, one containing 50 percent corn and 50 percent pentosan hydrolyzate and the other, 100 percent pentosan hydrolyzate fortified with corn steep liquor. Attempts to reduce the fermentation time by the use of these inocula were unsuccessful.

Engine Rating of Agricultural Motor Fuels By Standard Methods: (MFE-1-1 Revised)

Performance number gains were calculated from Research and Motor octane determinations of 3 alcohol-gasoline blends with 3 ml. of tetraethyl lead per gallon and varying amounts of sulfur. A 60 octane number reference fuel was used as base gasoline. The performance number scale is a more accurate measure of fuel quality than the non-linear octane scale. Results indicate that octane gains by alcohol are not effected by the presence of sulfur. (See Table II, Appendix.)

In connection with a cooperative project with the Oil Shale Demonstration Branch of the Bureau of Mines, United States Department of the Interior, Rifle, Colorado, the octane numbers of 3 shale gasolines, with and without tetraethyl lead, and with 2 concentrations of alcohol in the blend were determined. The results indicated that tetraethyl lead alone is not able to raise the octane numbers of the shale gasoline to that of a regular gasoline because of the adverse effects of sulfur. With the addition of 10 percent ethanol, however, and 3 ml. of tetraethyl lead, shale gasoline becomes a regular gasoline and with the addition of 25 percent ethanol a premium type gasoline is produced as far as octane number is concerned. (See Table III, Appendix.)

In an experiment to determine the influence of composition of gasoline on alcohol response, four base gasoline stocks were investigated. The best response with alcohol is found with straight-run and thermally cracked stock. (See Table IV, Appendix.)

Evaluation of Agricultural Motor Fuels by ASTM and Other Routine Chemical Tests and Operations: (MFE-1-2 Revised)

More than 650 determinations were made of tetraethyl lead, A.S.T.M. distillation, gravity, aniline point, Reid vapor pressure, viscosity (in connection with wear test), oxidation stability, gum, sulfur, aromatics and olefins.

Solubility of Light Hydrocarbons in Alcohols: (MFE-1-3 Revised)

The solubility of propane, iso-butane, and n-butane in ethanol were determined between 0° and 50° C. at various partial pressures of the gases. A summary of the results will be presented at the American Chemical Society Meeting in April in Cleveland, Ohio. This paper, "The Solubility of Propane and the Butanes in Ethanol," has been accepted for publication in the Journal of the American Chemical Society. Contrary to previous reports by G. Antonoff and coworkers, no evidence of a discontinuity in the thermal expansion coefficient of water and n-propanol was found. Also no slow change in the density of n-propanol with time was observed. The density of n-propane from 0° to 75° was measured very accurately and the data fitted to an equation. These results were summarized in a paper, "The Thermal Expansion of Water and n-Propanol," by Carl B. Kretschmer, which has been accepted for publication by The Journal of Physical and Colloid Chemistry.

Chemical Laboratory Studies of Suitability of Denaturants for Alcohol Fuels: (MFE-1-5)

Three additional denaturants "I," "J," and "K" were submitted to this Laboratory by the Alcohol Tax Unit for their suitability in agricultural motor fuels. (The composition of these denaturants is given in Table V, Appendix.) These denaturants in the prescribed concentrations are soluble in alcohol-water solutions containing up to 50 percent of water in a temperature range down to approximately -30° F. Any tendency towards corrosion can be checked by known inhibitors. All 3 denaturants, therefore, would be satisfactory for all practical purposes in automotive use.

Fundamental and Practical Studies on Corrosion of Metals by Agricultural Motor Fuels and on Corrosion Inhibitors: (MFE-1-6)

As a result of a large number of experiments, inhibitors suitable for the prevention of metal corrosion in alcohol-water mixtures were found. (See Table VI, Appendix.)

A summarization has been made of the data obtained on the corrosion of copper, zinc, aluminum, tin, iron, lead, nickel, Brass I* and Brass II** in anhydrous ethanol, 1 percent ethyl acetate in anhydrous ethanol, 1 percent acetaldehyde in anhydrous ethanol, 1 percent acetic acid in anhydrous ethanol, 95 percent ethanol, 1 percent ethyl acetate in 95 percent ethanol, 1 percent acetaldehyde in 95 percent ethanol, and 1 percent acetic acid in 95 percent ethanol. Weighed metal strips were immersed completely in sealed glass tubes for a period of six months. After exposure, the strips were re-weighed and the loss recorded. In several instances, attempts were made to identify the corrosion products. These results are being analyzed.

Lead is attacked in the presence of air by all solutions, though only to a minor degree by 95 percent and 85 percent ethanol-water mixtures. Solutions of 1 percent acetic acid in anhydrous ethanol, 95 percent ethanol, and benzene, and anhydrous methanol, particularly, are also corrosive towards lead in the absence of air; in all other cases the attack is either slight or negligible. Zinc is corroded by solutions of 1 percent of acetic acid in anhydrous and 95 percent ethanol, both in the presence and absence of air. Serious corrosion takes place also in mixtures of ethanol-methanol-water and ethanol-isopropanol-water. It appears that attack of both methanol and isopropanol on zinc is intensified in the presence of water. Brass I is attacked much more seriously by a 1 percent solution of acetic acid in anhydrous and 95 percent ethanol than is copper alone. This is also true for a 1 percent solution of acetic acid in benzene. Water intensifies the attack of a 1 percent solution of acetic acid in ethanol in both the presence and absence of air.

Effect of Compression Ratio and Supercharge on Alcohol Motor Fuels in Single Cylinder Engine: (MFE-1-7)

To establish a suitable engine procedure for investigating the behavior of alcohol motor fuels in supercharged engines, a considerable number of preliminary supercharged single-cylinder engine tests were made with a diisobutylene-toluene blend containing 10 percent ethanol. This work will be carried out at various compression ratios up to 50 inches absolute pressure, at optimum spark advance, at various air-fuel ratios, and at three engine speeds.

Engine Wear with High Sulfur Gasoline-Alcohol Fuels: (MFE-1-8)

Experimental work was continued on the effect of alcohol blends and alcohol-water injection on engine wear. The same automatic cycling procedure, namely, 3 minutes idling, 7 minutes road-load, and 5 minutes cooling to 50° F. was used. Results indicate that in all cases

*Brass I (Cu, 85.21; Zn, 14.783; Pb, .003; Fe, .004; Sn, Trace).
**Brass II (Cu, 94.27; Al, 5.38; As, .26; Fe, .05; Si, .04; and Pb, .003).

the presence of alcohol tends to reduce wear. (See Table VII, App.) This same finding, incidentally, was made in L-4 lubricating oil tests conducted at Armour Research Foundation under contract (RMA-127-12) on the effect of alcohol-water injection on additives contained in premium-type lubricating oils. The relatively low engine wear results obtained with 52-octane gasoline plus 3 ml. tetraethyl lead/gal. and with the same leaded gasoline in alcohol-water injection compared to previous runs with the Sohio fuel is no doubt due to the installation of the new block.

Attention is called to the fact that both 100-hour and 200-hour runs were made. It must be emphasized that all results are relative. The last two runs are made with oil-shale gasoline obtained by mutual agreement from the Oil-Shale Demonstration Plant, Rifle, Colorado.

Production and Utilization of Fungal Amylase: (E-3-2 and F-4-7)

Studies on the mode of action of dry fungal amylase preparations high in maltase activity, derived from a synthetic medium, showed that the breakdown of maltose by fungal maltase is probably effected by the conjoint action of α-glucosidase and transglycosidase. The disaccharide, maltose, is probably degraded to glucose in the following fashion: (1) A portion is hydrolyzed directly to glucose by the α-glucosidase, (2) a second portion is converted to glucose and a trisaccharide by the transglycosidase, (the trisaccharide has an α-1,4- and an α-1,6-glucosidic linkage), (3) the oligosaccharide is subsequently degraded to glucose and isomaltose by the α-glucosidase, and (4) the latter disaccharide is then hydrolyzed to glucose.

Studies were conducted in which fungal amylase was used as the converting agent in the fermentation of "sick" wheat to alcohol. The fungal amylase liquor was produced from wheat thin stillage with a solids content of 4 percent to which 5 percent of wheat had been added. Yields of alcohol from "sick" wheat with fungal amylase as the converting agent were equal to those obtained by the use of malt.

Fungal amylase was also used as the converting agent in an improved procedure developed for the "atmospheric" mashing of hard wheat. With the utilization of this procedure, it was possible to eliminate the operating difficulties usually encountered in the "atmospheric" mashing of wheat. Yields of 5.0 proof gallons per bushel of wheat were obtained by this method.

Pilot-plant experiments were conducted in an effort to reduce the time for fermentation of grain to alcohol with fungal amylase as the converting agent. Laboratory experiments had indicated that the addition of urea or ammonia to the mash would accomplish this result. In the pilot plant, when the mash was supplemented with 20 mg. of nitrogen per 100 ml. of mash, a yield of 5.1-5.2 p.g. per bushel of corn was obtained in 50-55 hours. Usually fungal amylase fermentations require 72 hours for completion. Urea, ammonium hydroxide, ammonium carbonate and diammonium phosphate are suitable sources of nitrogen for this purpose.

Feeding tests are being made by Bureau of Animal Industry of the by-product feeds derived from fungal amylase fermentations.

Publications

Production of Mold Amylases in Submerged Culture. II. Factors Affecting the Production of Alpha-Amylase and Maltase by Certain Aspergilli. By H. M. Tsuchiya, J. Corman, and H. J. Koepsell. Cereal Chem. 27 (4): 322-330. 1950.

Methods and Costs of Producing Alcohol from Grain by the Fungal Amylase Process on a Commercial Scale. By Production and Marketing Administration and Bureau of Agricultural and Industrial Chemistry. Technical Bulletin No. 1024, August 1950.

The Use of Fungal Amylase in the Industrial Production of Alcohol and Alcohol Products. By Richard W. Jackson, Russell H. Blom, and Henry M. Tsuchiya. 1950 Special Report of Lectures, Monographs and Reports given at Symposium on Recent Advances in the Fermentation Industries, at the University of St. Andrews, July 1949, published by the Royal Institute of Chemistry, pp. 93-107.

Note: Reports covering agricultural motor fuels research appear in the annual report on Agricultural Residues Utilization. They are also applicable here.

April 1, 1951 to June 30, 1952

Alcohol-Water Injection - Tractor Tests

Considerable trouble has been encountered with valves sticking and burning in farm tractors, particularly in Illinois, during postwar years. Some tractors must be overhauled several times a season because of this type of trouble. One of the major causes appears to be the use of regular gasoline—the prevalent fuel. As a possible means of preventing or alleviating valve-sticking and valve-burning in farm tractors, the use of alcohol-water injection is being studied under contract with the Department of Agricultural Engineering, University of Illinois, at Urbana. The 2-year contract calls for a performance comparison of three groups of tractors, each group operating under one of three sets of conditions: (1) Tractors with standard valves operating with aid of alcohol-water injection, (2) tractors with standard valves operating on standard fuel only, and (3) tractors with valve rotators, or special-type valves, operating on standard fuel only. Farm tractor operators in this test program, enlisted from Central Illinois farms, are required to keep complete records, over the contract period, on the operation and fuel consumption of their tractors. Special pieces of equipment and parts such as injectors, valve rotators, and special valves are supplied by the contractor to the farmers to make the tests. The contractor also furnishes the alcohol-water mixture; an attempt is being made to arrange for all participants to use the same type of lubricating oil so as to eliminate any variations in engine performance due to this factor. Since the contract was signed on November 16, 1951, 31 tractors out of the total of 60 required have been placed in operation. The period of operation to date is too short for significant results to be obtained. (u-1-1-34(C) (Rev.) (MFE) (pending))

To test under actual operating conditions the performance and fuel consumption of farm tractors in three engine compression ratio groupings using alcohol-water injection as an antidetonant, the Northern Laboratory has entered into a contract with the Ohio Agricultural Experiment Station at Columbus. Under this contract, farm tractor operators enlisted for participation in the test program are required to keep a complete record of the operation and fuel consumption of their equipment. Injectors and any necessary equipment for modifying tractor engines to give desired compression ratios are supplied by the contractor for the tests. The contractor also furnishes the alcohol-water mixture. There are now 50 tractors participating in this project, with compression ratios ranging from the low of 5.3:1 to the high of 7.9:1. Some are operating on alcohol-water injection, others are not—for comparison purposes. Only a few minor difficulties were encountered with injector malfunction, but improvements now

made should overcome any further difficulties. Average consumption of the 50:50 alcohol-water mixture used in the test was slightly over 2 percent of gasoline consumed, or about 1 gallon of alcohol to 100 gallons of gasoline. Twelve of the 15 farmers using high-compression engines in the test have indicated their desire to continue the use of injectors after the test program is completed. Their reasons for this are extra power and improved economy, with emphasis on the additional power. They estimated the gasoline consumption of high-compression engines, operated with aid of alcohol-water injection, to be 15 to 30 percent less than that of standard engines for the same work. (u-1-1-26(C) (MFE))

Alcohol-Water Injection - Lubricating Oil Studies

To determine whether injection of alcohol-water mixtures as an antidetonant in internal combustion engines would have adverse effect on premium-type lubricating oils containing additives, research on this problem was placed under contract several years ago with Armour Research Foundation at Chicago. This test program has been completed during this reporting period. Four widely distributed brands of additive-type lubricating oils and two non-additive oils were tested by means of the L-4 and FL-2 test procedures. The 36-hour L-4 test is to determine the oxidation and bearing corrosion characteristics of engine crankcase oils designed for use under heavy-duty service. The FL-2 test involves engine operation for a period of 40 hours at a more moderate speed (2500 r.p.m. against 3150 for the L-4), load, and oil temperature and with very low water-jacket temperatures to simulate conditions of moderate- or light-duty, intermittent service on the road. Weight loss in bearings was reduced significantly by the use of alcohol-water injection; the oils which gave the highest bearing loss without injection showed the largest degree of improvement with the use of injection. The two non-additive oils tested gave very high-bearing weight loss in the standard L-4 test when alcohol-water injection was not used. In the L-4 test of the two non-additive oils in which alcohol-water injection was used, one oil showed much improvement in bearing weight loss while the other oil proved to be worse in this respect. The purpose of testing non-additive oils at this point was to find out whether alcohol-water injection could take the place of additives in such oils. It would appear that this might apply to certain types of oils but much more work will have to be done to ascertain the necessary conditions. Since the tendency is toward use of additives in present-day lubricating oils, it is not considered worthwhile to pursue this problem further. FL-2 tests indicated no adverse effect of alcohol-water injection either with the four additive type or with the two non-additive type oils. In general, it may be said that alcohol-water injection will not interfere with the beneficial effect of additives in lubricating oils but may actually improve the performance of lubricating oils in regard to bearing weight loss and some other factors. (u-1-1-25(C) (MFE))

The study of the effect of alcohol-water injection on premium and heavy-duty lubricating oils when used with fuels containing either tetraethyl lead or relatively large amounts of sulfur was the subject of a research contract with the Southwest Research Institute, San Antonio, Texas. Interest in such tests with leaded gasolines was dictated by the present-day use of tetraethyl lead in gasoline; interest in results with high-sulfur gasolines came about because of the possibility during a national emergency of the need to use a lower grade of gasoline very likely containing larger amounts of sulfur. Seven test runs to determine the oxidation and bearing corrosion characteristics of an engine crankcase oil when various fuel combinations were used have been completed. Three of the tests were made with the use of alcohol-water injection and four without. These tests included runs, both with and without injection, using (1) a clear (non-leaded) gasoline, (2) the same clear gasoline plus 3 ml. of tetraethyl lead per gallon, and (3) the same clear gasoline with 0.15 percent sulfur. One additional test was made without injection using the same clear gasoline plus 3 ml. tetraethyl lead per gallon and 0.15 percent sulfur to note combined effect of the two materials in the fuel. In general, there was no essential difference in results with or without injection, although alcohol-water injection appears to reduce slightly the acidity of the lubricating oil. Engine sludge and varnish deposits on the cylinder walls appear to be unaffected. (u-1-1-27(C) (MFE))

Alcohol-Water Injection - Engine Tests

During investigation of the effects of alcohol-water injection on internal combustion engines, the action of two types of injectors was compared. One was the "old" flange-type manifold injector which operates on manifold vacuum and injects into the engine at a point below the carburetor an almost constant stream of antidetonant (alcohol-water mixture) regardless of the speed of the engine. The other type of injector, known as the "differential"-type, operates on both the manifold vacuum (in the lower engine speed range) and the carburetor venturi vacuum (at the higher engine speeds). It injects the antidetonant at the venturi. With the manifold injector, no economy in antidetonant consumption could be expected, since the flow is practically the same at all speeds. However, because the flow of antidetonant in the "differential"-type injector can be set to shut off at higher speeds where an octane number increases, and therefore injection is not needed, it should be possible to increase the mile-per-gallon rating of a given alcohol-water mixture using this injector. Alcohol-water injection using these two types of injectors was studied in road tests employing a GMC high-compression engine (8:1 compression ratio) in a "98" Oldsmobile. Tests were conducted at two initial spark settings and at various engine speeds ranging from 1000 to 3000 r.p.m. The fuel used for these comparative tests was a regular gasoline of 82 octane number.

The antidetonant consisted of 95 percent ethyl alcohol (95:5 alcohol-water mixture). In spite of over-injection at low engine speeds near 1000 r.p.m., the over-all antidetonant consumption by the use of the "differential"-type injector was significantly less than that of the flange-type injector, because of economical use of antidetonant at the higher engine speeds. Average miles-per-gallon values obtained amply illustrate this conclusion. For alcohol consumed, using the "differential"-type injector, a miles-per-gallon figure of 1160 was obtained. The corresponding value for the flange-type injector was 849. In these tests, the value for gasoline consumed was 18.1 miles per gallon for both types of injectors. The economy in antidetonant consumption made possible by use of the "differential"-type injector plus the difference in cost between a high-grade premium gasoline, required in the high-compression engine when injection is not used, and the regular gasoline which can be used with alcohol-water injection, should make injection attractive under these conditions. (u-1-1-4 (MFE))

The purpose of a study of engine operation with alcohol-water injection at low temperatures was to determine the effect of such operation on cylinder wear, corrosion, oil sludge formation, carbon formation, and general performance. These trials, made on four laboratory engines in a properly equipped cold room, were conducted under contract by the Corps of Engineers, Department of the Army, at Ft. Belvoir, Virginia. This project has been completed in this reporting period. Two engines were operated with alcohol-water injection and two without. All engines were operated on a 180-minute cycle which included, in succession, operation at simulated road load at 1000 r.p.m. engine speed, at wide-open throttle at 1400 r.p.m., again at 1000 r.p.m., idling, and finally a cooling-off period of 60 minutes. Duration of the tests varied from 1 to 2 1/2 weeks. Four different types of gasolines (clear and leaded gasoline, with and without sulfur) and two low-temperature lubricating oils were employed in these tests which were carried out at 0°, -20°, and -40° F. Tentative conclusions indicate that alcohol-water injection in internal combustion gasoline engines results in longer engine life at low temperatures when used with either leaded or unleaded fuel in comparison with engines not using the injection system. The longest engine life occurs when alcohol-water is used in conjunction with lightly leaded fuel. It is further concluded from these tests that the effect of the alcohol-water injection on the lubricating oil at low temperatures is not harmful. (u-1-1-21(C) (MFE))

To determine the feasibility of use, in military transport vehicles, of regular-grade, low-octane, straight-run gasoline with alcohol-water injection as an antidetonant, a contract was negotiated with the Ordnance Corps, the Department of the Army, at Aberdeen Proving Grounds, Aberdeen, Maryland. Tests under this contract were completed in this reporting period. In these tests, three 2 1/2-ton GMC trucks were used (vehicles numbered 205, 241, and 631).

Truck No. 205 was operated with a prototype 80-octane fuel only, representing a combat grade fuel expected to be available to the military during time of war. Vehicles 241 and 631 were operated with alcohol-water injection in combination with a 67-octane number, straight-run gasoline as the main fuel. The prototype 80-octane fuel conformed to specifications MIL-G 3056, but contained 0.3 percent of sulfur, oxidation inhibitor at the rate of 35 pounds per 1000 barrels of fuel, and from 2.52 to 3.12 ml. of tetraethyl lead per gallon to simulate impurity and additive contents of a wartime fuel. On the other hand, the lower octane fuel did not contain lead (critical item in war time) on oxidation inhibitor. This lower octane fuel, being free of extraneous material, would be expected to have cleaner burning characteristics in the engine than the protype 80-octane fuel, but could not be used alone because it had too low an octane number. By use of alcohol-water injection to boost the effective octane number of the lower octane fuel, good operating characteristics are obtained and there is no sacrifice of power output in the engine. The course over which the test trucks were driven was representative of military operating conditions, and consisted of a bituminous concrete highway, a gravel road, and a cross-country stretch. It was planned to drive the trucks for 12,000 miles or until engine breakdown occurred. Vehicle No. 205, operated on the prototype gasoline without injection, had two engine failures, one at 6,323 miles, and the second and final one at 8,861 miles, which necessitated replacement of exhaust valves. Vehicles 241 and 631, which used the 67-octane fuel aided by injection, ran without trouble for a total of 8,094 and 7,615 miles, respectively, at which time the test was terminated because of the second failure of vehicle No. 205. Incidentally, vehicle No. 631 had been operated for 2,541 miles on the prototype gasoline alone before starting the alcohol-water injection trial with 67-octane fuel. It was found that with the alcohol-water injection, detonation was completely suppressed and the use of the lower octane gasoline was feasible. Use of alcohol-water injection with the straight-run gasoline resulted in cleaner engines (less sludge, varnish, and combustion deposits) and less cylinder wear. (u-1-1-22(C) (MFE))

Engine-Wear Tests With High-Sulfur Fuels

This research program was undertaken to determine the effect of alcohol-water injection on cylinder wall wear when an internal combustion engine is operating on a high-sulfur gasoline. It is generally believed that in usual operation (without alcohol-water injection) cylinder wall wear is greater with a high-sulfur fuel than when more normal gasolines are used. Through a memorandum of understanding with the U. S. Bureau of Mines, a supply of high-sulfur gasolines from oil shale had been obtained for testing. Cylinder wall wear tests were made on (1) straight-run, unleaded, sulfur-free gasoline, (2) the same gasoline with sulfur added, and (3) shale oil gasolines containing varying proportions of sulfur.

Tests with these gasolines were run with and without the use of alcohol; alcohol was used both in blends with the gasoline and in injection mixtures with water. In all cases, the use of alcohol significantly reduced average cylinder wall wear. This project was completed during this reporting period. (u-1-1-15 (MFE)).

Dual Carburetion Studies

A possible alternative to the use of alcohol-water injection to allow the use in internal combustion engines of fuels with octane ratings below the engine requirements is the dual fuel carburetion system. The dual fuel carburetor operates on two fuels: a high-octane fuel to be used at or near full throttle (when higher power output is required of the engine), and a low-octane fuel used for moderate loads, the condition prevailing the majority of the operating time. The purpose of the special carburetor, which automatically switches from one fuel to the other as required, is to conserve the high-octane fuel by using it only when actually needed. The high-octane fuel can be a high-octane gasoline, a suitable alcohol-gasoline blend, or straight alcohol (anhydrous). In these experiments with a high-compression engine, straight alcohol, as well as mixtures of these alcohols with premium gasoline, were used on the high-octane side while the best grade of premium gasoline available was used for the low-octane side. To study dual fuel carburetion, road and dynamometer tests were made with a high-compression test engine of 10:1 compression ratio installed in a "98" Oldsmobile and equipped with EX104-66 Carter Dual Fuel Carburetor. The octane number requirement of this engine at full throttle was 100 at approximately 1000 r.p.m. engine speed. With a single fuel carburetion system, this engine would use 100-octane fuel under all operating conditions, but would require the full 100-octane rating of the fuel only under full-throttle conditions. It was determined that by using dual fuel carburetion this engine can be operated on a premium-grade gasoline of approximately 91-octane number on the low side of the carburetor, and would burn 100-octane fuel on the high side only a relatively small part of the operating time as required. It was found that the necessary high-octane fuel could be obtained by adding to the premium 91-octane gasoline 20 percent of ethyl alcohol. When using these two fuels, with dual fuel carburetion, alcohol consumption for average city and country driving conditions was from 1.4 to 1.6 percent of gasoline consumed, which is somewhat higher than that needed for alcohol-water injection under the same driving conditions. It is concluded that dual carburetion is less economical as far as agricultural motor fuels are concerned than alcohol-water injection.

Corrosion and Corrosion Inhibitor Studies

One of the problems involved in the use of alcohol as a motor fuel, either as a blend or by injection, is that of corrosion. Severe corrosion of the zinc-aluminum alloys employed in the fabrication

of carburetors has been observed. The corrosion has been found to be caused by residual NaCl in the dye used for coloring the alcohol fuel. It was important, therefore, to study the action of chloride ions on various metals in contact with ethyl and methyl alcohols, and with aqueous solutions of these two alcohols, to determine the mechanism of this type of corrosion and to find suitable measures to inhibit the reaction. Solutions containing one part per 10,000, 1 per 100,000, and 1 per million by weight of chloride ion were tested. Iron was not corroded in anhydrous ethyl alcohol either in the presence or absence of air. In the presence of oxygen, however, increasing the proportions of water in alcohol-water mixtures from 5 to 15 percent enhanced the corrosive action on this metal with increasing chloride ion concentration. In spite of the solubility of $FeCl_3$ in alcohol, neither ferrous nor ferric ions were found in the alcohol test solutions indicating the possible formation of complex compounds which remove these ions from action. Pure ethyl alcohol did not corrode aluminum. In the presence of chloride ions, however, corrosion did take place. Oxygen and water tended to repair the damage done by the chloride ion to protective oxide coatings on aluminum; more corrosion was observed in the absence of air than when air was present. In the absence of air, corrosion was so severe that specimens became perforated. Anhydrous methyl alcohol was much more corrosive than anhydrous ethyl alcohol. In methyl alcohol, a concentration of one part by weight of chloride ion per 10,000 caused complete disintegration of the aluminum test piece. As an important part of the corrosion problem, the mechanism of corrosion inhibition should be studied. Inhibitors which prevent corrosion in the injection system may present other unforeseen difficulties. During some recent experiments on the use of alcohol-water injection in farm tractors, the alcohol-water mixture employed was a commercial radiator antifreeze containing borax as a corrosion inhibitor. This mixture caused no corrosion of the injector system, but after it was used in the tractors for a short time the valves and valve stems were found to be coated with a greyish deposit consisting principally of sodium tetraborate (anhydrous form of borax). This emphasizes the care which must be taken in the selection of corrosion inhibitors. (u-1-1-13 (MFE))

Alcohol Denaturant Studies

If the use of alcohol-water injection in automotive or tractor engines should become general, alcohol used would necessarily have to be denatured to meet requirements of the Alcohol Tax Unit. Several special formulae found suitable as denaturants in alcohol used for injectors were not satisfactory to the Alcohol Tax Unit for general distribution to the public. Laboratory tests on three completely denatured alcohols, in which denaturants used were approved by the Alcohol Tax Unit, indicated that corrosion of

the injector parts caused by the denaturant substances could not be completely prevented with a sulfonated-oil-type corrosion inhibitor. Adjustment of the alkalinity, however, to about 8-9 pH improved the protective action of this type of inhibitor. Such solutions were tried for 30 days in commercial injectors and it appears that the extent of corrosion occurring under these circumstances would not interfere with operation of the injectors. Engine tests are now under way to investigate whether these mixtures will cause deposits on the engine valves and cylinder surfaces. (u-1-1-12 (MFE))

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Plant-Scale Tests on the Production of Ethyl Alcohol from Damaged Grains by the Fungal Amylase Process

Work on this project is being performed by the Grain Processing Corporation, Muscatine, Iowa under a research contract. Tests are being conducted to determine the practicability of the Northern Laboratory's fungal amylase process for the production of ethyl alcohol from damaged grain. Because the alcohol market has been unstable and the contractor has experienced difficulty in procuring damaged grain, work on the process has been delayed and it has been necessary to extend the termination date of the contract from May 23, 1953 to October 23, 1953.

Several tests have been conducted in which corn containing at least 50 percent damaged kernels has been fermented. In these runs, the yields of alcohol when fungal amylase was used as the converting agent compared favorably with those when malt was used. Additional tests will be conducted in which damaged corn, damaged wheat, and mixtures of these grains will be fermented. Although the results to date are not conclusive, it appears that fungal amylase may be substituted for malt in the production of alcohol from damaged grains with no decrease in yield. (u-1-1-31(C) (ED)).

Utilization of Flood-Damaged and Field-Germinated Wheat

During the disastrous flood in the Kansas City area in 1951, millions of bushels of wheat were flood damaged to such an extent that their use for livestock feeding was prohibited. The only means for salvaging the grain was its conversion to industrial alcohol. However, a number of distilleries which were engaged in this salvaging process, experienced difficulties in the fermentation of this material because the mashes did not ferment completely. Since flood disasters occur periodically and the problem of salvaging flood-damaged wheat will occur again, the alcohol productivity of this material was studied. In a series of laboratory experiments an average alcohol yield of 4.8-proof gallons per bushel was obtained using 10 percent of barley malt as the converting agent and basing the yield on a moisture content of 12.3 percent. This yield can be considered quite satisfactory because the alcohol yield of sound wheat under optimal practical conditions amounts to about 5.0-proof gallons per bushel.

A very interesting observation was made in these experiments which indicates that during the 3 months of deterioration only a small amount of the original starch was destroyed since the starch content on a dry basis was 68.4 percent which is of the same order of magnitude as for sound wheat. Evidently, during the spoiling process the wheat proteins are destroyed primarily, because the nitrogen content of the damaged wheat was found to be approximately 30 percent below that of sound wheat.

Field-germinated wheat is classified as damaged wheat and graded as sample grade. During field-germination the wheat loses some of its starch, but its β-amylase content shows large gains. Based on this phenomenon a mashing procedure was developed on a laboratory scale whereby the starch of field-germinated wheat was converted to fermentable sugars by means of the wheat amylases without the use of barley malt as a starch converting agent. The alcohol yield indicated a complete conversion of the starch to alcohol. The alcohol yields ranged from 4.8- to 5.3-proof gallons per bushel (56 pounds, dry basis). The variation in the yield was in accordance with the starch content, which ranged from 59 to 62 percent on a dry basis. (u-1-1-3 (Rev.) (ED) (discontinued)).

Alcohol-Water Injection - Deposit Formation

The octane requirement of engines increases with mileage until deposit equilibrium has been reached, when deposit formation and flaking-off proceed at about an equal rate. This equilibrium may be attained only in the combustion chamber since deposits may continue to accumulate on exhaust valves until burning or sticking occurs. Deposit accumulation can increase the octane requirement of an engine anywhere from 5 to 20 octane numbers. The Aberdeen test program, u-1-1-22(C), "Preliminary investigation on the use of alcohol-water injection in military transport vehicles" (discontinued), and other information appear to show that this increase in octane requirement of engines is less when injection is used. In order to obtain more conclusive evidence, experimental work on this problem is planned. An 8-cylinder V engine has been so arranged that its two sides can be run with different fuels and either with or without injection. By means of a "split timer" the spark advance of each of the 8 cylinders can be adjusted and controlled independently. This arrangement will enable the operator to follow the change of octane requirement, with and without injection, simultaneously, under identical engine running conditions and with considerable saving of fuel. No data have yet been obtained. (u-1-1-56 (MFE)).

Alcohol-Water Injection - Lubricating Oil Studies

The study of the effect of alcohol-water injection on premium and heavy-duty lubricating oils, when used with fuels containing tetraethyllead and sulfur, has now been completed. The work was carried out by the Southwest Research Institute, San Antonio, Texas, under a research contract. Two types of test procedures were used: The L-4 method, simulating high-temperature operation, such as sustained driving, heavy truck and tractor operation; and the FL-2 procedure, simulating conditions under which the engine never really warms up. The effect of

injection on four commercial lubricating oils (two premium and two heavy-duty type oils) was studied. The results of the L-4 tests did not indicate any significant difference in the presence or absence of injection and not even between the premium and the heavy-duty oils. The latter oils might be expected to give better performance. Slightly smaller amounts of engine deposits were formed, on the average, with injection and one premium lubricating oil. More significant results were obtained in the FL-2 tests, particularly in the "sludge total ratings." In all cases, the "sludge total rating" was better, and often markedly better, with alcohol-water injection than without. One of the heavy-duty oils produced slightly better ratings than the premium oils, but again the relative pattern remained. In all other respects, i.e., piston skirt and cylinder wall varnish, total varnish, and lubricating oil analyses, no constant pattern was established. It was evident that the lubricating oil was not as important a variable as might have been expected and that injection is not likely to interfere with efficient lubrication in the presence of lead and sulfur. (u-1-1-27(C) (MFE)).

Alcohol-Water Injection - Valve Burning and Sticking in Farm Tractors

Under a research contract, the Illinois Agricultural Experiment Station is supervising the operation of 60 tractors in order to determine the possible beneficial effect of alcohol-water injection on valve burning and sticking. Considerable delay was experienced in getting special valve parts and finding suitable cooperators in the immediate neighborhood of Urbana, Illinois. It was necessary, in order to eliminate as many variables as possible, to confine the test to two tractor makes and to a small number of gasoline and lubricating oil brands. Each tractor will be operated for a period of 2 years under the terms of the contract, the life of which has been extended to May 15, 1955.

Approximately 20 of the 60 tractors are using alcohol-water injection (50:50 alcohol-water mixture) and results will show whether injection, in addition to increasing the octane number, will also help to relieve the rather severe problem of valve burning and sticking. No conclusions can be drawn so far from the data on hand. (u-1-1-34(C) (MFE)).

Alcohol-Water Injection - Winter Operation of Motor Vehicles

The final report of the test program carried out by the Engineer Research and Development Laboratories, Corps of Engineers, Department of the Army, on the "preliminary investigation of the effect of alcohol-water injection on engine operation, using low-octane gasolines, at low temperatures" has now been received. Four commercial engines, two with and two without alcohol-water injection, were run in the low-temperature laboratory at Ft. Belvoir at temperatures ranging from zero to -40° F. The engines were operated in a cycle

designed to simulate conditions most likely to be encountered in winter service in town and on the farm. The conclusions of the final report check closely the tentative conclusions presented last year. Alcohol-water injection gave less wear on cylinders, main bearings, and rings, but slightly more wear on connecting rod bearings. Unleaded fuels produced less wear both with and without injection than leaded fuels. Alcohol-water injection did not affect performance characteristics, corrosion of internal parts, cylinder deposit, or lubricating oil additives. (u-1-1-21(C) (MFE)).

Alcohol-Water Injection - Tractor Engine Operation at Very High Compression Ratios

Laboratory experiments and subsequent field tests at Columbus, Ohio, indicate the practicability of operating tractor engines at compression ratios as high as 8:1 with injection. The farmers were delighted with the operation of these high-compression tractor engines. Because of the greater power available they were able to perform their work faster, easier, and at lower cost. It was of importance, therefore, to explore the possibilities of using still higher compression ratio farm tractor engines. Tractor engines have considerably higher octane requirements than automotive engines of the same compression ratio, and actual tests are needed to indicate whether injection can add the extra octanes needed. Two tractor engines of 8.6:1 compression ratio are available for the test program and work on one has just begun. (u-1-1-4 (Rev.) (MFE)).

Alcohol-Water Injection - Preignition

Preignition, as the word implies, is defined as ignition of the fuel-air mixture before it is ignited by the spark plug. Preignition, in contrast to knock, is not "explosive burning," but appears to form a definite flame front similar to normal ignition. Preignition usually takes place on the wall of the combustion chamber by a "hot spot," although it may also be initiated by suspended carbon or carbon-lead compound particles. Alcohols, olefins, and aromatic fuels have high octane numbers but will preignite under certain engine conditions more readily than isooctane, for example. It is becoming more and more apparent that preignition, rather than detonation, may be the limiting factor in the operation of high-compression engines. Melting of the piston crown or other damage to the piston appears to be a common consequence of severe preignition. It is of utmost importance, therefore, to investigate the factors underlying the preignition of alcohols and to find means to remedy such conditions. Under a research contract supervised by the Northern Laboratory, the Sloan Laboratories of Massachusetts Institute of Technology are now engaged in studying the surface conditions and other factors affecting preignition of alcohol fuels when used for power boost in military aircraft or as an antiknock in high-compression engines. An artificial "hot spot" consisting of an

insulated nichrome bar, the surface of which can be maintained at a uniform temperature, has been installed in a special single-cylinder engine. The temperature of this "hot spot" can be measured within the accuracy of ±20° C. by means of an optical pyrometer. Some preliminary motoring preignition tests have been performed, but no conclusions can be drawn from the data obtained so far. (u-1-1-35(C) (MFE)).

Alcohol-Water Injection - Gum Formation in Gasolines

In the comprehensive literature survey made by the Northern Laboratory in 1949, references were found to the isolated occurrence of increased gum formation in the presence of alcohol. These statements, of course, referred to the use of alcohols in blends but it was felt that gum formation might conceivably take place at an accelerated pace at the higher temperatures prevailing in the manifold during injection. Any gum formed in the manifold might deposit on the inlet valve and cause inlet valve sticking. The autoxidation of hydrocarbons is not always retarded by alcohols, and a reasonably thorough investigation was needed in order to find out the condition under which gum is likely to form in the presence of alcohol. Oxidation rates of tetralin, cyclohexene, di-isobutylene, and octene-1 and of mixtures of di-isobutylene with tetralin and cyclohexene were studied. Tetralin was chosen because its oxidation had been investigated extensively and it was thought that this would be of considerable help in the interpretation of the present work. This was found to be the case. Methyl, isopropyl, and _n_ and _tert_-butyl alcohol were studied in addition to ethanol. It was found that alcohols accelerated the oxidation of tetralin and cyclohexene but retarded the oxidation of di-isobutylene and octene-1. The oxidation of mixtures of di-isobutylene with tetralin and cyclohexene was also retarded in the presence of alcohols. The results were explained in terms of oxidation-chain reactions which gave a reasonable picture of the mechanism of gum formation. The work has been completed and the results indicate that no serious gum trouble will result when injection is used. (u-1-1-36 (MFE)).

Alcohol-Water Injection - Fuel Distribution Among Engine Cylinders

In the operation of multi-cylinder engines, gasoline is not distributed equally among the cylinders. In other words, each cylinder does not get the needed equal share of fuel. Since alcohol and water have high heats of vaporization and, therefore, tend to cool the air-fuel mixture, an accurate evaluation of their possible effect on fuel distribution is necessary.

Accurate data on the pressure-volume-temperature (p.v.t.) relationships of alcohols and other potential fuels from agricultural materials are needed in the calculation of their thermodynamic properties necessary for the evaluation of effect of injection on fuel distribution among engine cylinders and, in general, for calculating the theoretical efficiencies of internal combustion engines. A close search of the literature revealed the practical nonexistence of p.v.t. data for these substances. Empirical correlations that have been customarily used for alcohols have recently been shown to be grossly inaccurate. A program for measuring the p.v.t. relationships of agricultural fuels was, therefore, undertaken. Special apparatus has been constructed and data have been obtained for ethanol and methanol of a temperature range from 40° to 120° C. at pressures up to 1 atmosphere. The results indicate that the gas imperfections are considerably larger and also more complicated in form than those calculated from the customary empirical correlations mentioned earlier. This resulted in correspondingly larger corrections in the calculated thermodynamic functions. (u-1-1-36 (MFE)).

<u>Alcohol-Water Injection - Tractor Tests</u>

The project,carried out by the Ohio Agricultural Experiment Station under a research contract, to test the practicability of using alcohol-water injection in farm tractors, has been successfully completed. Four different makes of tractors, including two models of one of the makes, making a total of 50, were selected and operated on farms in the Columbus, Ohio area. Displacements (cylinder volumes displaced by piston movement) ranged from 152 to 284 cu. in., which covered fairly well the range of tractor sizes on farms. Octane gains ranged from 14 octane numbers for the 5.3:1 compression ratio tractor to 7 for tractors of 8:1 compression ratios. In terms of improvement in engine performance, these gains are equivalent, since the octane scale is not linear. By increasing the compression ratio 1.5 numbers, power would be increased by 10 to 20 percent, depending upon the engine design. Engine manufacturers are now also increasing the power by increasing the engine speed and displacement, with small increases in compression ratio. Alcohol-water injection rates averaged 3.8 percent by volume of the gasoline consumed. There was remarkably little variation in the <u>average</u> amount of injection in all compression ratio groups. Injection rates were an excellent measure of the way the farmer operated his tractor. Some farmers tended to load their tractors to the very limit, as indicated by injection rates as high as 14.6 percent, while others seldom reached full-load as shown by a .90 percent rate. Twenty-five tractors with compression ratios from 6.5:1 to as high as 8:1, were operated for 1 year with no failures. Six of the engines were disassembled after the test period and were found to be in good condition (other parts of the tractor were not inspected). During the severe part of the winter, some of the high-compression engines could not be started with the standard battery.

Two of the tractors with compression ratios of 8:1, equipped with an additional battery, in parallel with the regular one, could be started at any time. Twelve-volt batteries are rapidly becoming standard equipment in the higher compression passenger cars. A few cases of bent plow beams and twisted shafts in power-take-off equipment were reported. These cannot be considered the fault of the extra engine power, but they illustrate the fact that judgment is required for proper use of the more powerful engines.

The increase in power and smoothness of operation was of more importance to farmers than the saving in fuel. Farmers were able to handle heavier loads, and sometimes to operate in a higher gear ratio with a saving in time. Twenty-three of the 25 tractors, in which the compression ratio was increased for the test program, will continue to be used by the farmers. The only complaint mentioned was the handling of the alcohol-water mixture in addition to regular fuel, and this was considered to be a minor objection. From an economy point of view, standard compression ratios probably would not be advantageous. Some farmers reported that their standard engines ran smoother and had more "lugging" power, similar to operation on a damp or rainy day. The underlying principle here is that the pressure of moisture displaces a certain amount of air and thus increases the proportion of fuel to air. If the carburetor was set too lean, increased power would result. The power output of other engines was materially increased, because the carburetors did not permit an adjustment of the air-fuel mixture for maximum power output on gasoline alone. The alcohol thus provided the extra fuel needed in addition to improving the octane number. One farmer used unleaded, straight-run gasoline with alcohol-water injection in his tractor engine. When comparing this engine with others using regular gasoline, it was found that the combustion chamber and valves of this engine were remarkably clean, which would tend to prolong engine life and extend satisfactory performance. The results of this test have aroused considerable interest among tractor manufacturers. (u-1-1-26(C) (MFE)).

Corrosion and Corrosion Inhibitor Studies

It is generally assumed that acetic acid is formed in the combustion of alcohol in internal combustion engines, and the implication is frequently made that alcohol, therefore, is more corrosive than hydrocarbon fuels. Even though no adverse effects of this nature had been found under actual operation conditions, it was felt that direct experimental evidence was needed to support this finding. Various components of gasolines (diisobutylene, cyclohexane, isooctene, benzene, and isooctane), commercial gasolines, and shale gasolines, containing various amounts of sulfur, with or without alcohol or lead, were run at three fuel-air ratios (lean, stoichiometric, and rich). At the end of each run, the exhaust products were analyzed for aldehydes and total acids. The results, so far obtained, show that the acidity of the exhaust condensates of diisobutylene, isooctane, cyclohexane, and regular gasoline increased

when going from rich to lean mixtures. Addition of 25 percent ethanol decreased the amount of acidity in the exhaust in every case. The acidity and aldehyde curves for absolute ethanol showed a maximum value, at intermediate air-fuel-ratios, differing, therefore, from the behavior of hydrocarbons. The highest acid values were found with straight methanol. It was not surprising, therefore, to find that a blend of regular gasoline containing 21 percent methanol and 4 percent ethanol gave larger acid values than the gasoline alone. The ethanol was added to prevent separation of the mixture. The conclusions, to be drawn from the data so far obtained, are that ethanol produces less acidity in the exhaust condensate while methanol produces more than do the hydrocarbon fuels. These data will be correlated with those previously obtained on engine wear tests conducted at the Northern Laboratory. Work on the controlled corrosion of zinc in alcohol solutions is being continued. Arrangements are being made to follow the changes by means of X-ray analysis in order to explain the corrosion maxima found.(u-1-1-59) (MFE)).

Agricultural Motor Fuels

Alcohol-water injection for farm tractors. John D. Hummell, Department of Agricultural Engineering, Ohio Agricultural Experiment Station, and Richard Wiebe, NRRL. U. S. Dept. Agr. AIC-349, 12 pp. (Processed). February 1953.

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Alcohol-Water Injection--Distribution of Alcohol Among Engine Cylinders

Gasoline and mixtures of gasoline and alcohol are not distributed equally among the various engine cylinders because of a difference in the physical characteristics of these fuels, and also because of certain structural features of the carburetor and engine manifold which preferentially direct the air-fuel mixture in one or more directions. In order to obtain needed experimental data for a theoretical calculation of the effect of alcohol-water mixtures on the gasoline-air mixture in the manifold, pressure-volume-temperature relationships were determined for the three lower primary alcohols: methyl, ethyl and isopropyl. The results obtained from the measurements of vapor densities agreed very satisfactorily with those obtained from vapor heat capacities and from the heats of vaporization. As a further contribution to the solution of the problem, previous experimental data on the vapor liquid composition of alcohol-gasoline mixtures were analyzed thermodynamically. The equations derived were in satisfactory agreement with vapor-pressure data for several alcohol-gasoline systems. For mixtures of alcohols with aromatic hydrocarbons in the liquid state, it is necessary to assume that each alcohol monomer or polymer can combine with one molecule of hydrocarbon. The information obtained is required to permit calculations of the degree to which the different fuel components are present in the true vapor form or the droplet form in the engine manifold. (u-1-1-36 (MFE))

Alcohol-Water Injection--Preignition in Automotive Engines

Preignition is here understood as ignition of the air-fuel mixture by "hot spots" located on cylinder walls, valve and piston surfaces, spark plugs, or any other part of the combustion chamber. The "hot spot" acts like an additional spark plug and the flame front, which originates at the "hot spot," appears to be propagated in an exactly similar fashion. Under a research contract, the Sloan Laboratories for Aircraft and Automotive Engines of Massachusetts Institute of Technology have made measurements of preignition temperatures of n-heptanes, isooctane, diisobutylene, benzene, ethanol, methanol, and blends of n-heptane with xylidine and methyl aniline as a function of speed, inlet temperature and pressure and air-fuel ratio. Increase of intake air temperature and pressure lowers the temperature at which preignition occurs, while the opposite is true when the engine speed is increased. These data are preliminary to those that will be obtained later to show the effect of alcohol on the preignition temperatures of these hydrocarbons. Decreasing the size of the "hot spot" increases the preignition temperature, indicating that heat transfer is an important factor in the mechanism of preignition. (u-1-1-35(C) (MFE))

Alcohol-Water Injection--Valve Sticking and Burning in Farm Tractors

Work under a research contract, in which the Illinois Agricultural Experiment Station is supervising the operation of farm tractors in order to determine the possible beneficial effect of alcohol-water injection on valve burning and sticking, is continuing and will not be completed until late spring 1955. Out of a total of 60 tractors, 36 are still operating, but no final conclusions can be drawn until all tractors have been checked out and the records examined. Unfortunately, however, engine failures also occurred for extraneous reasons which indirectly affect valve life, such as leakage of antifreeze through the head gasket. Such occurrences invalidate the test results for the particular tractor. Difficulties with dust clogging the alcohol-water injectors have been remedied by connecting air bleed lines to the atmosphere through the engine air intake filter. (u-1-1-34(C) (MFE))

Alcohol-Water Injection--Effect of Deposits on the Knocking Tendencies of Engines

There appears to be considerable evidence that chemical compounds, such as formaldehyde, acetaldehyde, and peroxides, formed ahead of the flame front (precombustion reaction) are the precursors of the chemical reaction terminating in engine knock. Although it will be impossible to isolate the extremely unstable free radicals by methods used here, precombustion reactions may give indirect information from which useful conclusions may be drawn. Results obtained from such experiments would form the basis for an understanding of the effect of alcohol-water injection on deposit formation. These deposits increase the knocking tendencies of engines or, in other words, they increase the octane requirements. For the purpose of obtaining information on precombustion reactions, an apparatus has been assembled, consisting of a single-cylinder variable compression-ratio engine and a condenser train into which part of the pre-combustion products are passed and condensed for later analysis. Pre-flame conditions are simulated through high inlet air and jacket temperatures, and high-compression ratios. Preliminary runs have been made to establish satisfactory operation of the apparatus. (u-1-1-56 (MFE))

Alcohol-Water Injection--Corrosion of Metals by Alcohol-Water Mixtures

Zinc is one of the metals used in the construction of alcohol-water injectors and accessories. It was necessary, therefore, to investigate its possible corrosion by alcohol-water in mixtures. The study of the corrosion of zinc has yielded results of considerable complexity. The corrosion maxima found in the past, at certain alcohol concentrations, could not be reproduced accurately in spite of all precautions taken in maintaining identical experimental conditions, (temperature, "surface," concentration).

Preliminary X-ray data gave no indication of a change in crystal structure of the corrosion products with different alcohol concentrations. These products were identified principally as zinc oxide with some β-zinc hydroxide. Metals, which are thermodynamically (electrochemically) unstable in water and alcohol, may not corrode if the corrosion product formed is insoluble and covers the surface uniformly with a protective layer. Whether or not this layer will be protective cannot be predicted from thermodynamic data since it depends on surface conditions and the physical state of any insoluble corrosion product formed. Except at very high alcohol concentrations, zinc corrosion products do not form a uniform layer but leave active (anodic) centers at which the corrosion process continues. It is entirely reasonable to suppose, therefore, that the formation of active centers is haphazard. This is indicated by the variable rate of corrosion. However, the results confirm in general that corrosion rates are higher in solutions of low alcohol concentration than in water and that corrosion is negligible in high concentrations of alcohol in water and absent in straight alcohol. Hydrogen-ion (pH) measurements revealed the interesting fact that the pH of the alcohol solution in the presence of zinc rose from 7, the approximate equilibrium value for β-zinc hydroxide, to within a range of 9 to 11. This is equivalent to an increase of hydroxide ion concentration of 100- to 10,000-fold. It was found that the negatively charged colloidal suspension of presumably zinc hydroxide was stable only in the presence of metallic zinc. Soon after the metal was removed, the pH began to drop and gradually approached the equilibrium value after 30 days or more. Investigations are now under way to study the effect of this transient pH on the corrosion of zinc since it may give a clue regarding a way to inhibit zinc corrosion in alcohol solution. It is known that the "additional" pH caused by colloidal suspensions may have a chemical activity equivalent to that of ordinary hydrogen and hydroxide ions. (u-1-1-59 (MFE))

Alcohol-Water Injection--Tractor Engine Operation at Very High Compression Ratio

Brake horsepower and specific fuel consumption of a commercial farm tractor engine "B", operating with alcohol-water injection, were determined at compression ratios of 5.9:1, 6.76:1 and 8.52:1 as a function of speed, spark advance, and manifold pressure at constant air-fuel ratio. At the manufacturer's setting of 31° spark advance, and 1450 r.p.m., brake horsepower increased by 10.5 percent and specific fuel consumption (lb. of fuel/bhp hr.) decreased by 18.3 percent when going from a compression ratio of 5.9:1 to one of 8.52:1. This is not quite as spectacular as the corresponding figures of 27 percent and 26.6 percent for another farm tractor "A", operating with alcohol-water injection, in which the compression ratio was raised from 5.3:1 to 8:1.

However, in the latter case the combustion chamber of the tractor engine was designed for the high-compression ratio while in the tractor engine "B" high altitude pistons were used to obtain the highest ratio. Another factor which reduced the effectiveness of tractor engine "B" was the large jump in frictional horsepower between compression ratios of 6.76:1 and 8.52:1. Octane requirement of tractor "B" at 1300 r.p.m. and 1450 r.p.m. was lowered from 99.5 and 97.0 octane numbers, respectively, to only 97 and 93.3 when retarding the spark from 30° to 20°, the approximate limit of stable operations. A 10 percent alcohol blend with a premium gasoline of 92.7 octane numbers or injection of a 50:50 alcohol-water mixture at a rate of 20 percent at <u>full throttle</u> using this same premium as base fuel, satisfied the octane requirement of tractor "B" at the highest compression. This indicates that alcohol is needed before a tractor of such high-compression ratio can be operated unless, of course, liquified petroleum gas is used. (u-1-1-4 (Rev.) (MFE))

Alcohol-Gasoline Blends

Preliminary investigations have been made of anti-knock properties, fuel consumption, and vapor lock in automotive engines using alcohol-gasoline blends containing 10 to 25 percent alcohol. A 10-percent addition of alcohol to commercial regular and premium gasolines increased the laboratory octane ratings from 84.3 to 90.0 and from 91.7 to 94.2, respectively. A 25-percent addition raised the octane level to 96.8 and 98.4, respectively. Road octane ratings indicated that in the very high octane range and with high alcohol blends (25 percent) in particular, the octane numbers of the blend may drop more rapidly with increased speed than does the octane requirement of the engine. This indicates the possibility of high-speed knock which will be investigated further. Very carefully conducted fuel consumption tests with a 1953 Chevrolet automobile showed that fuel consumption may not increase significantly when a blend is used and no change is made in the carburetor setting. The 10-percent blend gave an increase in fuel consumption of 1.34 percent while the 25-percent showed a decrease of 0.43 percent. Acceleration was better with the blends than without. A road test procedure for vapor lock was worked out, closely resembling that approved by the Coordinating Research Council and the one used by a major oil company. Theoretical equations for the volatility of alcohol-hydrocarbon mixtures were formulated and will be checked experimentally. (Exploratory (MFE))

Agricultural Motor Fuels

Practical experiences with alcohol-water injection in trucks and farm tractors. Richard Wiebe and John D. Hummell. Agr. Eng. 35 (5): 319-326 (1954).

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ALCOHOL-WATER INJECTION-- EFFECT ON VALVE STICKING AND BURNING IN TRACTORS AND PREIGNITION IN AUTOMOTIVE ENGINES

Summary Statement:

One of the principal mechanical troubles experienced in farm-tractor operation is valve sticking and burning. Uncontrolled preignition can also cause severe damage in automotive engines. Under a contract, a study was made by the University of Illinois to determine the effect of alcohol-water injection on valve life in tractors burning regular and unleaded white gasoline, in field operation on Illinois farms. Under another contract, Massachusetts Institute of Technology conducted tests to determine the effect of alcohol-water injection on preignition in internal-combustion engines.

Alcohol-water injection when used with regular (leaded) gasoline was found to have no effect on valve life. This is because deposits accumulate in the engine during idling or low-load operation when no injection takes place, and the small amount of alcohol-water injected during heavy-load operation is not able to dislodge or modify deposits already formed by the combustion of leaded gasoline. However, the use of alcohol-water injection allows low-octane, unleaded white gasoline to be used in tractor engines which would otherwise require regular gasoline. The rate of deposit formation and the occurrence of valve failures were greatly reduced in the tractors operated on unleaded white gasoline with alcohol-water injection. (N1 1-34(C) (AP)).

Alcohol-water injection was found to counteract the pronounced tendency of n-heptane, representing the low-octane components of gasoline, to preignite at low speeds and high intake pressures, and did not increase the preignition tendency of any of the other classes of compounds normally present in gasoline. These results indicate that the addition of alcohol either by injection or by blending with the gasoline would not increase the tendency for preignition to occur in high-compression internal-combustion engines. (N1 1-35(C) (AP)).

These studies on alcohol-water injection have been completed and no further work on alcohol as a motor fuel, other than that covered by line projects N1 1-89, "Determination of road and laboratory performance characteristics of alcohol-gasoline blends in passenger cars, trucks, and tractor engines," and N1 1-90, "Laboratory determination of the physical properties and stability of alcohol-gasoline motor fuel blends," is contemplated at this time.

Publications: None.

Physical Properties of Alcohol-Gasoline Blends.

The rapid changes in the composition of modern gasolines, particularly their great increase in volatility, required a comprehensive laboratory investigation of the compatibility of alcohol with present high-octane gasolines. Reid vapor pressure and vapor-liquid ratios of approximately 100 commercial gasolines and special fuels with and without alcohol were determined for correlation with road performance. When these fuels were tested on the road, it was found that the temperature at which the vapor-liquid ratio equals 30 (t_{30}) will serve as a criterion for the susceptibility of a fuel to vapor lock. It was further shown that any fuel having a value of t_{30}, which is less than 37° F. above the ambient temperature, would develop vapor lock in the test car. Since alcohol blends will have a greater volatility, its t_{30} will be lowered. For equal performance, the gasoline for blending with alcohol must have a lower Reid vapor pressure than most gasolines used commercially. Since methyl and isopropyl alcohols are being used to prevent icing of carburetors at temperatures just above freezing in damp or foggy weather, the use of ethyl alcohol for this purpose was investigated. The laboratory tests of this investigation dealt with the possible losses of alcohol which may be encountered in storage and distribution. A careful investigation was made of the stability of ternary mixtures of ethyl alcohol-water-2,2,4-trimethylpentane and ethyl alcohol-water-1-octene at 0° and 25° C. Check measurements were also made of previous determinations of the system ethyl alcohol-water-benzene. Since 2,2,4-trimethylpentane or isooctane, 1-octene, and benzene are representatives of three of the major constituents of gasoline, a prediction can be made regarding the distribution of alcohol-gasoline blends in the two phases when separation occurs. Tables and diagrams have been prepared to show the limits of stability, particularly those of 10 and 25 percent alcohol-gasoline blends, as well as of the composition of the two phases. From these measurements it was shown by means of examples what losses of alcohol may be expected to occur under storage and distribution unless proper precautions are taken. Work under this project has been completed. (N1 1-90 (AP) Discontinued).

Road Performance of Alcohol-Gasoline Blends.

Although alcohol-gasoline blends have been used as a motor fuel for more than 30 years in various parts of the world, difficulties in their use, especially in connection with vapor lock and octane requirements of modern engines, have been and are still being encountered because of incomplete knowledge of the compatibility of present-day gasolines with alcohol. A vapor lock criterion for alcohol motor fuels was established by testing approximately 100 fuels with or without alcohol in a vehicle on the road under approved test conditions. It was found that the temperature at which the vapor-liquid ratio equaled 30 (t_{30}) was an excellent criterion and results showed that any fuel having a

value of t_{30} which is less than 37° C. above ambient temperature will cause vapor lock in the test car. Carburetor icing observations were conducted with a 1951 six-cylinder, passenger-car engine. Provision was made for controlling the temperature of the air by mixing it with warm laboratory air, and for controlling its humidity by injecting steam. It was found that 2 percent of ethyl alcohol added to commercial winter gasolines is somewhat more effective than 2 percent of isopropyl alcohol, ordinarily used in commercial gasolines, in reducing carburetor icing. Extensive performance tests were conducted on two tractor engines having compression ratios ranging from 5.9 to 8.5:1. Horsepower, specific fuel consumption and octane requirements were determined using 3 hydrocarbon fuels and 13 blends including straight alcohol. Alcohol blends may be used in high-compression engines which have compression ratios too high for presently available commercial gasolines. The higher possible power output might compensate for the higher fuel consumption in farm operations where the greater load capacity is often an important factor in saving time during planting and harvest operations. Work under this project has been completed. (N1 1-89 (AP) Discontinued).

Publications:

Stability of Alcohol-Gasoline Blends. Janina Nowakowska, Carl B. Kretschmer, and Richard Wiebe. Boletin de la Asociacion Nacional de Ingenieros Agronomos III(70): 3-7. (1956).

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